Published in final edited form as:
Environ Sci Technol. 2012 February 21; 46(4): 2033–2039. doi:10.1021/es202942q.

Impact of the Deepwater Horizon oil spill on bioavailable polycyclic aromatic hydrocarbons in Gulf of Mexico coastal waters

Sarah E. Allan, **Brian W. Smith**, and **Kim A. Anderson***
Environmental and Molecular Toxicology Department, Oregon State University, ALS 1007, Corvallis, OR 97331

Abstract

An estimated 4.1 million barrels of oil and 2.1 million gallons of dispersants were released into the Gulf of Mexico during the Deepwater Horizon oil spill. There is a continued need for information about the impacts and long-term effects of the disaster on the Gulf of Mexico. The objectives of this study were to assess bioavailable polycyclic aromatic hydrocarbons (PAHs) in the coastal waters of four Gulf Coast states that were impacted by the spill. For over a year, beginning in May 2010, passive sampling devices were used to monitor the bioavailable concentration of PAHs. Prior to shoreline oiling, baseline data were obtained at all the study sites, allowing for direct before and after comparisons of PAH contamination. Significant increases in bioavailable PAHs were seen following the oil spill, however, pre-oiling levels were observed at all sites by March, 2011. A return to elevated PAH concentrations, accompanied by a chemical fingerprint similar to that observed while the site was being impacted by the spill, was observed in Alabama in summer, 2011. Chemical forensic modeling demonstrated that elevated PAH concentrations are associated with distinctive chemical profiles.

INTRODUCTION

On April 20th, 2010 a lethal explosion at the *Deepwater Horizon* oil drilling rig located 66 km southeast of the Louisiana coast in Mississippi Canyon Block 252, led to the largest marine oil spill in United States history. Estimates of the amount of oil spilled into the ocean vary, however the Federally accepted estimate of 4.1 million barrels of oil (7.0×10^5 m^3) has been supported by independent researchers [1]. Furthermore, an estimated 2.1 million gallons of dispersants were applied at the ocean surface and wellhead [2].

The oil that flowed from the Macondo well during the Deepwater Horizon oil spill contained approximated 3.9% polycyclic aromatic hydrocarbons (PAHs) by weight; an estimated 2.1×10^{10} g of PAHs were released during the spill [3]. PAHs are one of the principal contaminant classes of concern in oil spills because many compounds are toxic and/or carcinogenic to humans and wildlife. The water solubility and volatility of PAHs decreases as their molecular weight increases; however, low water concentrations of PAHs can be environmentally relevant due to their potential to bioaccumulate in organisms [4, 5]. In the case of marine oil spills, such as the Deepwater Horizon spill, there is an initial, acute risk to organisms that can become covered in viscous crude as well as acute and chronic risks from

*Corresponding Author: kim.anderson@orst.edu, Phone: 541-737-8501, Fax: 541-737-0497.

SUPPORTING INFORMATION AVAILABLE

Additional information about the methods used to calculate dissolved PAH concentrations in water are presented in supporting information. Figures that present the full characterization of PAH chemical profiles for all samples are also included in this section. This information is available free of charge via the Internet at http://pubs.acs.org/.

exposure to toxic chemicals through air, water and food. Even after the oil is no longer visible, chemicals of concern can persist in the environment [6] and affect exposed organisms [5, 7]. It is the freely dissolved fraction of chemicals in the water that is bioavailable to diffuse across biological membranes and enter organisms and the food web [8]. The use of chemical dispersants during the Deepwater Horizon oil spill was a source of contention among scientists and the public, in part because the application of dispersants to crude oil makes PAHs and other hydrophobic compounds more soluble in water, increasing their bioavailability [9–12].

Passive sampling devices (PSDs) were developed to address the issue of quantifying the bioavailable fraction of hydrophobic compounds in environmental media. They sequester and accumulate the freely dissolved, and therefore bioavailable fraction of hydrophobic organic contaminants, such as PAHs; mimicking passive uptake and accumulation of these compounds by biomembranes and lipid tissues [13]. PSDs provide a time integrated measure of the concentration of chemicals in the environment and, by effectively sampling a large volume of water, allow for the detection of chemicals that are present at low concentrations [13]. Fortifying PSDs with performance/permeability reference compounds (PRCs) prior to field deployment allows for an accurate determination of sampling rates, which can be used to calculate the bioavailable concentrations of chemicals in the water [13, 14]. Polyethylene membrane PSDs have been applied in a range of environmental media [13, 15–19] including monitoring PAHs in petroleum-contaminated water [20–24]. More recently, variants of the semi-permeable membrane device (SPMD) sampler that do not contain triolein have been developed and validated [15, 25–27]. These lipid-free tubing (LFT) PSDs are cheaper and require less clean-up prior to analysis than SPMDs.

This objective of this study was to assess the impact of the Deepwater Horizon oil spill on bioavailable PAHs at coastal sites in Gulf of Mexico. Baseline data from coastal waters was collected prior to the oil reaching any of the study sites. As a result, direct before-and-after comparisons of PAH contamination can be made. A recognized lack of pre-spill data has hindered efforts to understand the environmental impacts and fate of oil from the Deepwater Horizon spill [28]. This research provides unique pre-oiling data for study sites in four Gulf Coast states. Understanding spatial and temporal changes in bioavailable PAHs provides information about potential exposures to contamination that can be broadly applied to many areas including biology, ecology, public health and seafood safety in the Gulf of Mexico. A second objective was to apply forensic chemistry modeling techniques to elucidate sources of the bioavailable chemicals of concern that were observed before, during and after the oil spill.

MATERIALS AND METHODS

Sample Collection

Lipid-free tubing PSDs were constructed from low-density polyethylene tubing and fortified with perdeuterated performance/permeability reference compounds (PRCs) using methods described elsewhere [29, 30]. Briefly, additive-free tubing was cleaned with hexanes to remove potential analytic interferences, the tubing was heat sealed at one end, then the PRCs were injected into the interior of tubing and it was sealed at the other end. The final dimensions of each sampler are 2.6 cm wide by 1 m long. PSDs were stored in sealed Teflon bags until use and storage stability quality control samples were maintained throughout the study.

Stainless steel cages containing five PSDs were deployed from piers in coastal marine waters. One set of samplers, infused with PRCs, was deployed at each site during each sampling event. Sampling cages were suspended in the water column, at least 1 m above the

bottom. Water depths varied by site and tide cycle between 2–8 m. PSDs can sequester contaminants that are not freely dissolved in the water column if the sampler membrane comes in direct contact with non-aqueous phase media, such as oil sheens or droplets. To avoid this, precautionary measures were taken to prevent contact of the sampling material with crude oil floating on the surface of the water during deployments. When surface oil or sheen was visible, samplers were lowered into the water sealed in plastic bags that were removed after the samplers were secured below the surface in the water column. Based on visual inspection of the samplers upon retrieval from the water and results that show dissolved concentrations below solubility limits for all analytes in all samples, there is no evidence that the samplers in this study were ever superficially contaminated by oil.

Samplers were deployed at four sites: Grand Isle, Louisiana, Gulfport, Mississippi, Gulf Shores, Alabama and Gulf Breeze, Florida (Figure 1). The site at Grand Isle, LA was located the closest to the source of the spill and had little natural or human-devised physical protection from the influence of Gulf of Mexico waters during the oil spill. The site in Gulfport, MS was afforded limited protection from oiling by offshore barrier islands, which were heavily oiled during the spill. The sampling sites in Bon Secour, AL and Gulf Breeze, FL were at the mouths of Mobile Bay and Pensacola Bay, respectively. They were more protected from direct oiling than the other sites because of the natural peninsulas that delimit the bays as well as the booms that were put in place to protect those areas. All of the sites are impacted, to varying degrees, by local urban and industrial activities, which highlights the importance of having pre-oiling baseline data for comparison when determining the impacts of the spill on these coastal waters.

These sites were chosen based on the Mississippi Canyon Trajectory Forecasts that the National Oceanic and Atmospheric Administration (NOAA) began producing after oil was observed on the surface of the ocean. Basic geography and information about dominant ocean currents in the Gulf of Mexico were also taken into consideration. Additional criteria for site selection included their accessibility to researchers and protection for sampling equipment from theft and vandalism. All four research sites are located in shallow, coastal waters and are accessed by piers or docks.

The first sampling event began on May 10th, 2010 and was completed prior to shoreline oiling at any of the study sites. A total of nine sampling events were conducted over the course of more than a year (names in quotes refer to the shorthand used in text and figures): ‘May 2010’ (May 10–13, 2010), ‘June (1)’ (June 8–11, 2010), ‘June(2)’ (June 11–July 7, 2010), ‘July’ (July 7–August 5, 2010), ‘August’ (August 5–September 8, 2010), ‘September’ (September 8–October 13, 2010), ‘March’ (February 9–March 15, 2011), ‘April’ (March 15–April 29, 2011), ‘May 2011’ (April 29–June 8, 2011). Samplers were not recovered from Grand Isle, LA in July, 2010. Sampling deployment times varied throughout the study due to practical considerations involving travel, weather and site accessibility, as well as other factors. The first deployment, in May, 2010, was limited to four days because of projected impending shoreline oiling at the site in Grand Isle, LA and an interest in obtaining pre-oiling data at all sites. The sampling period in early June was limited to four days because of concern about the samplers becoming saturated at sites that were being heavily oiled. Analysis of those samples indicated that longer deployment periods could be used for the remainder of the study. Because PRCs were used to calculate uptake rates it was not necessary for the deployment times to be the same throughout the study or for the samplers to reach equilibrium.

Sample Preparation

PSDs were retrieved from the field and transported to the laboratory at Oregon State University. Samplers were transported at ambient temperature in sealed Teflon bags. Storage

stability studies, conducted prior to this research, verified that transport of PSDs in sealed Teflon bags at ambient temperatures (up to 50 °C) for up to two weeks does not result in a significant loss of PAH analytes. Transportation quality control samples, fortified with PRCs and PAH analytes, were used throughout the study. Recoveries of PAH analytes and PRCs from storage stability samples and fortified trip blanks did not exceed ±10% of the true value.

In the laboratory, the samplers were cleaned with hydrochloric acid and isopropanol to remove superficial fouling, mineral salts and water [13]. Perdeuterated PAH surrogate recovery standards were spiked on the PSD samplers prior to extraction to allow for verification of extraction efficiency and recovery correction. The 5 PSDs from each cage were extracted together as one sample to increase detection capabilities. Samplers were extracted by dialysis in *n*-hexane using methods detailed elsewhere [26]. Briefly, samplers were immersed in 200 mL of *n*-hexane for 4 hours, the dialysate was decanted, then dialysis was repeated for 2 hours and the dialysates were combined. Samples were quantitatively concentrated to a final volume of 1 mL.

Chemicals

Solvents used for pre-cleaning, clean-up and extraction were Optima® grade or better (Fisher Scientific, Pittsburgh, PA). The following 33 PAH analytes were included in analyses: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, 1-methylphenanthrene, 2-methylphenanthrene, 3,6-dimethylphenanthrene, anthracene, 2-methylanthracene, 9-methylanthracene, 2,3-dimethylanthracene, 9,10-dimethylanthracene, fluoranthene, pyrene, 1-methylpyrene, retene, benz(a)anthracene, chrysene, 6-methylchrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene and dibenzo(al)pyrene. The perdeuterated PAH compounds used as PRCs were fluorene-D10, p, p′-DDE-D8and benzo(b)fluoranthene-D10. The following perdeuterated PAHs were used as surrogate recovery standards: naphthalene-D8, acenaphthylene-D8, phenanthrene-D10, fluoranthene-D10, pyrene-D10, benzo(a)pyrene-D12 and benzo(ghi)perylene-D12; and perylene-D12 was the internal standard.

Sample Analysis

PSD extracts were analyzed using Agilent 5975B Gas Chromatograph-Mass Spectrometer (GC-MS); with a DB-5MS column (30 m × 0.25 mm × 0.25 μm) in electron impact mode (70 eV) using selective ion monitoring (SIM). The GC parameters were as follows: injection port maintained at 300 °C, 1.0 mL min^{-1} helium flow, 70 °C initial temperature, 1 min hold, 10 °C min^{-1} ramp to 300 °C, 4 min hold, 10 °C min^{-1} ramp to 310 °C, 4 min hold. The MS temperatures were operated at 150, 230 and 280 °C for the quadrupole, source and transfer line respectively. Sample concentrations were determined by the relative response of the deuterated surrogate to the target analyte in a nine point calibration curve with a correlation coefficient greater than 0.98.

Quality Assurance/Control

Over 30% of the total number of samples analyzed in this study corresponded to quality control samples, which included PSD fabrication blanks, field and trip blanks for each deployment/retrieval, laboratory clean-up blanks and reagent blanks. All target compounds were below the detection limit in all blank quality control samples.

Mean surrogate standard recoveries varied between 48–102% for naphthalene-D8 and benzo(g, h, i)perylene-D12 respectively. Lower recoveries were observed for 2–3 ring PAHs, which are relatively volatile, due to losses during sample preparation, especially sample concentration. Target analytes were recovery corrected, following analysis, based on the measured recovery of the surrogate with the most similar structure. The average relative standard deviation (RSD) for all analytes from replicate samples was 7.5%. Naphthalene had the highest RSD; averaging 21%. This variability is attributed to differences in losses during the sample concentration steps and is not significantly different from RSDs observed during the 500:1 concentration of surrogates overspiked in *n*-hexanes.

The method detection limits for PAH analytes in samples obtained from a composite of 5 PSDs was 10 pg/uL. This translates into detection limits ranging between 0.001–0.05 ng/L for individual PAH compounds in water. Calibration curves had a fit that was greater than 0.98 for all analytes in the method. Calibration verification standards for target analytes, surrogates and PRCs were analyzed at least every 10 samples and reported values within ±15% of the true value were considered acceptable. Only results from samples run between two calibration verifications that met the quality control criteria were accepted.

Water Concentration Calculation

Water concentrations were calculated using the empirical uptake model with PRC-derived sampling rates [13, 31, 32]. The equations used to calculate the water concentrations presented in this study are detailed in the Supporting Information. This model is based on uptake kinetics and does not require any assumptions about individual analytes being at equilibrium or in the linear uptake range. The use of PRCs allows for an accurate determination of *in situ*, site-specific sampling rates under variable exposure conditions, including variable temperatures, flow rates and biofouling [31]. Additionally, it is not necessary for the analytes of interest to reach equilibrium with the sampler in order to determine sampling rates [13]; therefore, variable sampling deployment times are feasible. Fluorene-D10, benzo(b)fluoranthene-D10 and p, p′-DDE-D8 PRCs were used in the calculations. PAH compounds and p, p′-DDE have similar compound specific effects on sampling rates [13]; therefore water partitioning coefficients for these compounds can be calculated with the same equation, based on log K_{ow}. These PRCs cover a range of log K_{ow} values that makes them adequate for deriving the uptake rates of the PAH analytes included in this study [31]. When PRC recoveries were below 20% or above 80%, the sampling rates were determined using an improved model for calculating *in situ* sampling rates when recoveries approach 0 or 100% [14] (details provided in Supporting Information).

Data Modeling

For comparisons of total PAHs, all 33 PAH analytes were summed. Two-way comparisons between different sampling events at the same site were performed using the Wilcoxon signed-rank test. For sums and two-way comparisons, analyte concentration values below the detection limit were equal to zero. Probabilities less than p=0.05 were considered significant.

Confidence intervals were calculated for graphical representation of the data and are reported in the results. Numerous replication studies performed by this laboratory, in diverse environments, over the last ten years have demonstrated that PSDs give highly reproducible results; the variability in the data is consistent and predominantly a result of sample processing and analysis. Due to practical considerations it is often unfeasible to deploy replicate samplers. In these cases, the measured concentrations of analytes are representative only of the specific sampling location; the confidence interval is calculated based on pooled variance from replication pilot studies and represents a statistically defensible measure of

variance around the reported value. In this study, the reported values were measured in the environment and the confidence intervals are calculated measures of methodological variance. The interpretation of the results should be limited to the areas where direct measurements were made.

For other analyses, data were standardized to avoid a magnitude bias when analyzing chemical profiles. Sample measurements were scaled to reflect relative abundances by representing individual analyte concentrations as percentages of the total PAHs measured in a given sample.

Principal component analysis (PCA) is a multivariate variable reduction technique in which principal components (PCs) are calculated as combinations of the original variables. The goal of PCA is to express as much of the total variation as possible with a few uncorrelated PCs. Use of PCA can reveal important features obscured within the original data and has been applied to PAH fingerprinting and allocation studies [23, 33]. In this case PCA was used to explore similarities, differences and changes in chemical profiles of samples obtained from the study sites over the course of more than a year. PCA was performed using all of the analytes from each sample. The resulting PCs were analyzed graphically for apparent similarities and differences between samples including spatial and temporal tendencies.

SAS 9.2 (SAS Institute Inc.) was used for statistical analyses and modeling. Graphics were created using Sigma Plot 11.0 (Systat Software Inc.).

RESULTS AND DISCUSSION

Bioavailable PAHs in Coastal Waters of Four Gulf Coast States

The sum of the measured bioavailable water concentrations of all 33 PAH analytes considered in this study is denoted as Σ_{33}PAH. Prior to shoreline oiling at Grand Isle, LA, the measured Σ_{33}PAH in May, 2010, was 3.8 (±0.64) ng/L. Samplers were in the water column during heavy shoreline oiling in the month of June (samples June-1 and June-2), during which time the highest concentrations of Σ_{33}PAH measured in this study were recorded. The maximum concentration of 170 (±14) ng/L, which was significantly greater than the initial baseline measurement ($p<0.001$), was observed in the June-1 sample. The concentration decreased from the observed maximum in June-2 ($p=0.049$) to 140 (±8.4) ng/L, which was still significantly greater than the pre-oiling observation ($p=0.004$). The samplers at Grand Isle were lost in the month of July. The Σ_{33}PAH concentration at the site decreased in August and September but remained significantly elevated. By March, 2011, Σ_{33}PAH was not significantly different from pre-oiling levels ($p=0.098$) and this trend was maintained through the conclusion of the study (Figure 2).

During the first sampling event in Gulfport, MS the Σ_{33}PAH was 7.3 (±0.41) ng/L. This increased to 21 (±1.3) ng/L in June-1, at which time the site was being visibly impacted by oil, and remained significantly elevated above the initial observation during June-2 and July ($p<0.05$). From August 2010 through May 2011, none of the samples taken at this site demonstrated Σ_{33}PAH concentrations greater than pre-oiling measurements ($p>0.05$) (Figure 2).

The temporal progression of bioavailable PAHs at the site in Gulf Shores, AL demonstrated a different trend than the other sites. The Σ_{33}PAH concentration at the site was 9.1 (±0.50) ng/L in May 2010 and did not change significantly until July ($p=0.0005$) when it reached 20 (±1.3) ng/L. The concentration remained significantly elevated above pre-impact levels ($p<0.002$) through September, when a maximum concentration for the site, 26 (±2.8) ng/L,

was observed. The Σ_{33}PAH concentration in March, 2011 was not different from the initial observation at the site ($p=0.112$); however, samples from April and May, 2011 showed significantly elevated Σ_{33}PAH concentrations ($p<0.008$) that were comparable ($p>0.100$) to samples taken from the site during the oil spill (Figure 2). This observed increase in bioavailable PAHs may be due to re-suspension of contaminated sediments related to recorded high wind events and/or continued near-shore clean-up activities, both of which were observed during those sampling periods. It could also be explained by increased inputs from other sources and/or other climactic factors.

The coastal water at Gulf Breeze, FL had an initial Σ_{33}PAH concentration of 3.9 (±0.16) ng/L. No significant change in this concentration was observed until August, 2010, when it reached 16 (±1.2) ng/L and remained significantly higher through September ($p<0.001$). A significant decrease from the maximum observed concentration was recorded in March, 2011 ($p<0.001$) and bioavailable PAHs were not different from pre-spill levels at this site in April or May of 2011 ($p>0.30$) (Figure 2). Although oil was reported to have washed up on Pensacola Beach and in Gulf Islands National Seashore on June 23, 2010, an increase in bioavailable PAHs was not observed at the study site until August. This site, at the mouth of Pensacola Bay, was protected from direct oiling, which is apparent in the contrast between the timing of oil sightings in the near vicinity and the observed PAH concentrations. This highlights the potential for significant differences in impacts on a reduced spatial scale in the coastal area.

A west-to-east trend in the timing of the maximum recorded PAH concentrations was observed; the western sites were impacted by increased bioavailable PAHs earlier than the more eastern sites. This timing is explained by the distance of the sites from the well head as well as the influence of the oceanic loop current, which flows clockwise around the Gulf of Mexico towards Florida. A west-to-east decreasing trend in the magnitude of the maximum recorded bioavailable PAHs was observed. The site at Grand Isle, LA was the most heavily impacted in June, 2010, the sites in Gulfport, MS and Gulf Shores, AL shows similar magnitudes of PAHs when they were being impacted and lower maximum PAH concentrations were observed at the site in Gulf Breeze, FL. This is likely explained by dispersion and ageing of the PAHs from the spill, which increase with distance from the source.

It is important to note that the ng/L, or parts per trillion, concentration levels observed in this study refer only to the freely dissolved fraction of chemicals in the water column, which does not include oil slicks, tar balls, suspended droplets or any other undissolved fractions. To the authors' knowledge comparable data on dissolved PAHs in the Gulf of Mexico following the Deepwater Horizon oil spill is not available at this time. Reported values of total PAHs in water samples ranged from over 100 μg/L near the wellhead, during the spill to below detection limit [34]; however differences in the PAH analytes included in the analysis, the sampling methods and the detection limits make it impossible to do a direct comparison. The concentration of bioavailable PAHs determined in this study are comparable to those estimated from fish tissue concentrations following the Exxon Valdez oil spill. Neff and Burns [35] estimated that the concentration of dissolved PAHs in Snug Harbor after the spill was between 237–291 ng/L based on salmon carcass tissue or 4690 ng/L based on mussel tissue. Given the distance between the wellhead and the nearest sampling site in this study, lower observed concentrations of PAHs than those seen in other studies where samples were taken closer to the source of the oil spill [36], are expected.

Estimating exposure and bioaccumulation using PSDs

Bioavailable water concentrations represent what an organism in the water column would be exposed to through passive partitioning. Partitioning across gill membranes and integument

is the dominant rout of uptake for fish and shellfish [7, 8], although dietary contributions should not be discounted, especially for high trophic level predators and chemicals with log K_{ow}'s greater than 5.5 [37]. Because PAHs bioaccumulate in organisms, the concentration of these compounds in biological tissues will be much greater than in the surrounding water; likely more similar to mass:mass concentrations in the PSD itself, which are in the μg/kg to mg/kg range [38]. This is thought to be especially true for invertebrates, such as bivalves and crustaceans, which do not readily metabolize PAHs [38].

Σ_{33}PAH concentrations in PSD samplers in this study ranged from 68.5–6030 μg/kg. These concentrations are comparable, within an order of magnitude, to tissue concentrations that were measured in seafood from the Gulf of Mexico following the Deepwater Horizon oil spill. The US FDA reported mean total PAH concentrations of 3676 μg/kg in oyster tissue, 411 μg/kg in crab, 56.9 μg/kg in shrimp and 21–143 μg/kg in a variety of finfish [39]. Additionally, the PAH concentrations in PSDs in this study are comparable, within an order of magnitude, to salmon and mussels tissue concentration observed in the Gulf of Alaska following the Exxon Valdez oil spill [35]. PAH concentrations in PSDs could be applied, as a measure of potential exposure, to ecological and human health risk models [38].

Source Modeling – Chemical Profile PCA

Principal component analysis (PCA) was used to explore similarities, differences and changes in the chemical profiles of samples obtained from the study sites. PCA is a multivariate variable reduction technique in which principal components (PCs) are calculated as combinations of the original variables in order to express the maximum total variation with a few uncorrelated PCs. This modeling approach has been applied to PAH fingerprinting and allocation studies [23, 33, 40].

There are a number of trends that were revealed during visual analysis of the PCA output from this data (Figure 3). Prior to shoreline oiling at any of the sites (May 2010; month 1), the chemical profiles at all four sites were similar and group closely on the PCA figure. For the three sites that were not impacted in June-1; Gulf Shores, AL and Gulf Breeze, FL, the chemical profiles for month 2 also group closely with month 1. During shoreline oiling in Grand Isle, LA, the chemical profiles of the samples from that site changed (months 2 and 3), as shown by the distancing of these points from the baseline observation on the PCA plot. There is no data for month 4 at the Grand Isle, LA site. Interestingly, in months 5 and 6, the concentration of PAHs at Grand Isle, LA had decreased significantly from the maximums observed in June and July but the chemical profile remained similar, as seen by the proximity of these four observations. This suggests an attenuation of the input but a similar source. The other three sites were impacted by oiling throughout the year and showed a tendency for PAH chemical profiles from the sampling events with the highest recorded concentrations to be most distant from the pre-oiling observations. However, the PAH assemblage that impacted the more easterly shorelines had a different chemical profile than what was seen in Grand Isle, LA, likely due to aging of the oil and relatively more significant inputs from other sources. The tendency for the chemical profiles at these three sites to change in the same way, as demonstrated by their closely grouped temporal displacement in the same direction on the PCA plot, suggests at least one similar, significant source. Analysis of other PCs, especially PC 3 (not shown), suggests that inter-state differences are a secondary contributor to variability in the data set. Full PAH chemical profiles are available in the Supporting Information.

Samples from Gulf Shores, AL, taken in April and May, 2011, (months 8 and 9) when a renewed increase in PAH concentrations was observed, group closely with samples taken when the site was being visibly impacted by oil (Figure 3). This supports the hypothesis that oil from the Deepwater Horizon spill may still be affecting this site. Local authorities in

Gulf Shores report visible contamination of near shore sediments with oil and continued oiling of the shoreline. Cleaning crews were working in the Bon Secour area of Gulf Shores, removing oiled sand from the beaches, through the end of this study. The elevated PAH levels recorded at this site in April and May, 2011, suggests that at least a fraction of the remnant oil is bioavailable and therefore a consideration for environmental and human health risks. There is a need for continued monitoring of remnant oil and dissolved PAHs in the Gulf of Mexico.

CONCLUSION

This study demonstrates that the Deepwater Horizon oil spill impacted coastal waters of the Gulf of Mexico and contributed to temporary increases in the bioavailable concentration of PAHs. It provides a unique record of pre-oiling, baseline concentrations of PAHs at coastal sites in four Gulf of Mexico states. This responds to a recognized need for pre-spill data [28] and allows for direct before-and-after comparisons to be made. Furthermore, this data provides measures of potential exposures to PAHs in ecologically sensitive coastal areas, accessed by large human populations, which can be incorporated into on-going studies in a variety of fields. The persistently elevated levels of contamination at Gulf Shores, AL, observed after a decrease to pre-oiling levels, merit further study. Though this study demonstrates a nearly complete attenuation of Deepwater Horizon oil inputs by the one year anniversary of the spill at three of the four coastal sites, it does not preclude contamination of sediments or other media not contemplated here nor the possibility that residual oil could become re-suspended and dissolved in the water column.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This project was supported in part by award numbers P42 ES016465 and the associated Analytical Chemistry Facility Core, P30 ES000210 and R21 ES020120 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the National Institutes of Health. We appreciate valuable help from Steven O'Connell, Lane Tidwell, Kevin Hobbie and Glenn Wilson. We would like to thank Grand Isle State Park (scientific collection permits from the Louisiana Office of State Parks), Gulfport Harbor, Bon Secour National Wildlife Refuge (permit numbers 10-011 and 11-002) and Gulf Shores National Seashore (permit numbers GUIS-2010-SCI-0022 and GUIS-2011-SCI-0042).

References

1. Camilli R, Di Iorio D, Bowen A, Reddy CM, Techet AH, Yoerger DR, Whitcomb LL, Seewald JS, Sylva SP, Fenwick J. Acoustic measurement of the Deepwater Horizon Macondo well flow rate. Proceedings of the National Academy of Sciences. 2011
2. Kujawinski EB, Kido Soule MC, Valentine DL, Boysen AK, Longnecker K, Redmond MC. Fate of Dispersants Associated with the Deepwater Horizon Oil Spill. Environmental Science & Technology. 2011; 45(4):1298–1306. [PubMed: 21265576]
3. Reddy CM, Arey JS, Seewald JS, Sylva SP, Lemkau KL, Nelson RK, Carmichael CA, McIntyre CP, Fenwick J, Ventura GT, Van Mooy BAS, Camilli R. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. Proceedings of the National Academy of Sciences. 2011
4. Albers, PH. Petroleum and Individual Polycyclic Aromatic Hydrocarbons. In: Hoffman, DJ.; Rattner, BA.; Burton, AG.; Cairns, J., editors. Handbook of ecotoxicology. 2. CRC Press LLC; Boca Raton, FL: 2003. p. 342-360.

5. Carls MG, Thedinga JF. Exposure of pink salmon embryos to dissolved polynuclear aromatic hydrocarbons delays development, prolonging vulnerability to mechanical damage. Marine Environmental Research. 2010; 69(5):318–325. [PubMed: 20089299]
6. National Research Council. Oil in the Sea III: Inputs, Fates and Effects. National Academies Press; Washington, DC: 2003. p. 280
7. Carls MG, Holland L, Larsen M, Collier TK, Scholz NL, Incardona JP. Fish embryos are damaged by dissolved PAHs, not oil particles. Aquatic Toxicology. 2008; 88(2):121–127. [PubMed: 18479765]
8. Connell, DW. Bioaccumulation of xenobiotic compounds. CRC Press Inc; Boca Raton, FL: 1990. p. 232
9. Hemmer MJ, Barron MG, Greene RM. Comparative toxicity of eight oil dispersants, Louisiana sweet crude oil (LSC) and chemically dispersed LSC to two aquatic test species. Environmental Toxicology and Chemistry. 2011 In Press, Corrected Proof.
10. Ramachandran SD, Hodson PV, Khan CW, Lee K. Oil dispersant increases PAH uptake by fish exposed to crude oil. Ecotoxicology and Environmental Safety. 2004; 59(3):300–308. [PubMed: 15388269]
11. Singer MM, George S, Lee I, Jacobson S, Weetman LL, Blondina G, Tjeerdema RS, Aurand D, Sowby ML. Effects of Dispersant Treatment on the Acute Aquatic Toxicity of Petroleum Hydrocarbons. Archives of Environmental Contamination and Toxicology. 1998; 34(2):177–187. [PubMed: 9469860]
12. Wolfe MF, Schwartz GJB, Singaram S, Mielbrecht EE, Tjeerdema RS, Sowby ML. Influence of dispersants on the bioavailability and trophic transfer of petroleum hydrocarbons to larval topsmelt (Atherinops affinis). Aquatic Toxicology. 2001; 52(1):49–60. [PubMed: 11163430]
13. Huckins, JN.; Petty, JD.; Booij, K. Monitors of organic chemicals in the environment: semipermeable membrane devices. Springer; New York: 2006. p. 223
14. Booij K, Smedes F. An Improved Method for Estimating in Situ Sampling Rates of Nonpolar Passive Samplers. Environmental Science & Technology. 2010; 44(17):6789–6794. [PubMed: 20701278]
15. Allan IJ, Booij K, Paschke A, Vrana B, Mills GA, Greenwood R. Field Performance of Seven Passive Sampling Devices for Monitoring of Hydrophobic Substances. Environmental Science & Technology. 2009; 43(14):5383–5390. [PubMed: 19708370]
16. Bonetta S, Carraro E, Bonetta S, Pignata C, Pavan I, Romano C, Gilli G. Application of semipermeable membrane device (SPMD) to assess air genotoxicity in an occupational environment. Chemosphere. 2009; 75(11):1446–1452. [PubMed: 19289247]
17. Vrana B, Allan IJ, Greenwood R, Mills GA, Dominiak E, Svensson K, Knutsson J, Morrison G. Passive sampling techniques for monitoring pollutants in water. TrAC Trends in Analytical Chemistry. 2005; 24(10):845–868.
18. Wells, JB.; Lanno, RP. Passive sampling devices (PSDs) as biological surrogates for estimating the bioavailability of organic chemicals in soil. In: Greenberg, BM.; Hull, RN.; Roberts, MHJ.; Gensemer, RW., editors. Environmental toxicology and risk assessment: science, policy and standardization -implications for environmental descisions. Vol. 10. American Society for Testing and Materials; West Conshohocken, PA: 2001. p. 253-270.
19. Seethapathy S, Górecki T, Li X. Passive sampling in environmental analysis. Journal of Chromatography A. 2008; 1184(1–2):234–253. [PubMed: 17719053]
20. Harman C, Farmen E, Tollefsen KE. Monitoring North Sea oil production discharges using passive sampling devices coupled with in vitro bioassay techniques. Journal of Environmental Monitoring. 2010
21. Carls MG, Rice SD, Marty GD, Naydan DK. Pink Salmon Spawning Habitat is Recovering a Decade after the Exxon Valdez Oil Spill. Transactions of the American Fisheries Society. 2004; 133(4):834–844.
22. Thomas RE, Lindeberg M, Harris PM, Rice SD. Induction of DNA strand breaks in the mussel (Mytilus trossulus) and clam (Protothaca staminea) following chronic field exposure to polycyclic aromatic hydrocarbons from the Exxon Valdez spill. Marine Pollution Bulletin. 2007; 54(6):726–732. [PubMed: 17328928]

23. Wang, Z.; Stout, SA. Oil Spill Environmental Forensics. Academic Press; San Diego, CA: 2007.
24. Røe utvik TI, Durell GS, Johnsen S. Determining Produced Water Originating Polycyclic Aromatic Hydrocarbons in North Sea Waters: Comparison of Sampling Techniques. Marine Pollution Bulletin. 1999; 38(11):977–989.
25. Adams RG, Lohmann R, Fernandez LA, Macfarlane JK, Gschwend PM. Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. Environmental Science & Technology. 2007; 41(4):1317–1323. [PubMed: 17593736]
26. Anderson KA, Sethajintanin D, Sower G, Quarles L. Field trial and modeling of uptake rates on in situ lipid-free polyethylene membrane passive sampler. Environmental Science & Technology. 2008; 42:4486–4493. [PubMed: 18605575]
27. Carls MG, Holland LG, Short JW, Heintz RA, Rice SD. Monitoring polynuclear aromatic hydrocarbons in aqueous environments with passive low-density polyethylene membrane devices. Environmental Toxicology and Chemistry. 2004; 23(6):1416–1424. [PubMed: 15376527]
28. Ramseur, JL. Deepwater Horizon Oil Spill: The Fate of the Oil. Congressional Research Services; 2011. p. 22
29. Anderson KA, Sethajintanin D, Sower G, Quarles L. Field Trial and Modeling of Uptake Rates of In Situ Lipid-Free Polyethylene Membrane Passive Sampler. Environmental Science and Technology. 2008; 42(12):4486–4493. [PubMed: 18605575]
30. Sower GJ, Anderson KA. Spatial and Temporal Variation of Freely Dissolved Polycyclic Aromatic Hydrocarbons in an Urban River Undergoing Superfund Remediation. Environmental Science & Technology. 2008; 42(24):9065–9071. [PubMed: 19174872]
31. Huckins JN, Petty JD, Lebo JA, Almeida FV, Booij K, Alvarez DA, Cranor WL, Clark RC, Mogensen BB. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. Environmental Science & Technology. 2001; 36(1):85–91. [PubMed: 11811495]
32. Lohmann R, Muir D. Global Aquatic Passive Sampling (AQUA-GAPS): Using Passive Samplers to Monitor POPs in the Waters of the World1. Environmental Science & Technology. 2010; 44(3): 860–864. [PubMed: 20104908]
33. Boehm, PD. Polycyclic Aromatic Hydrocarbons (PAHs). In: Morrison, RD.; Murphy, BL., editors. Environmental Forensics Contaminant Specific Guide. Academic Press; San Diego, CA: 2006. p. 313-337.
34. Boehm, PD.; Cook, LL.; Murray, KJ.; Royer, L. Distribution and fate of PAH and Chemical Dispersants in the Water Column Following the Deepwater Horizon OIl Spill. Society of Environmental Toxicology and Chemistry Conference, (poster); Boston, MA. 2011.
35. Neff JM, Burns WA. Estimation of polycyclic aromatic hydrocarbon concentrations in the water column based on tissue residues in mussels and salmon: An equilibrium partitioning approach. Environmental Toxicology and Chemistry. 1996; 15(12):2240–2253.
36. González JJ, Viñas L, Franco MA, Fumega J, Soriano JA, Grueiro G, Muniategui S, López-Mahía P, Prada D, Bayona JM, Alzaga R, Albaigés J. Spatial and temporal distribution of dissolved/ dispersed aromatic hydrocarbons in seawater in the area affected by the Prestige oil spill. Marine Pollution Bulletin. 2006; 53(5–7):250–259. [PubMed: 16274705]
37. Landrum PF, Eadie BJ, Faust WR. Toxicokinetics and toxicity of a mixture of sediment-associated polycyclic aromatic hydrocarbons to the amphipod Diporeia sp. Environmental Toxicology and Chemistry. 1991; 10(1):35–46.
38. Allan SE, Sower GJ, Anderson KA. Estimating risk at a Superfund site using passive sampling devices as biological surrogates in human health risk models. Chemosphere. 2011; 85(6):920–927. [PubMed: 21741671]
39. Gohlke JM, Doke D, Tipre M, Leader M, Fitzgerald T. A Review of Seafood Safety after the *Deepwater Horizon* Blowout. Environmental Health Perspectives. 2011; 119(8)
40. Oug E. Multivariate Approach to Distribution Patterns and Fate of Polycyclic Aromatic Hydrocarbons in Sediments from Smelter-Affected Norwegian Fjords and Coastal Waters. Environmental Science & Technology. 1997; 31(5):1253–1258.

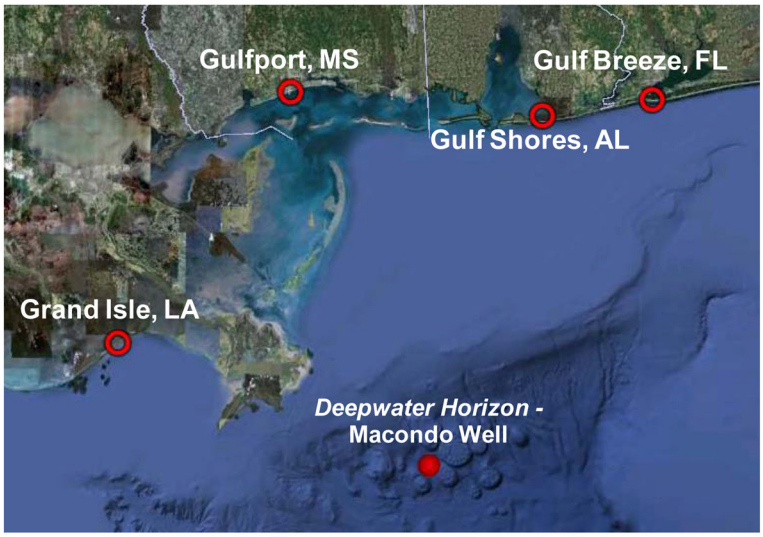

Figure 1. Sampling locations at four states in the Gulf of Mexico

Sampling sites are indicated by open circles. The location of the *Deepwater Horizon* rig and Macondo well is shown with a solid circle.

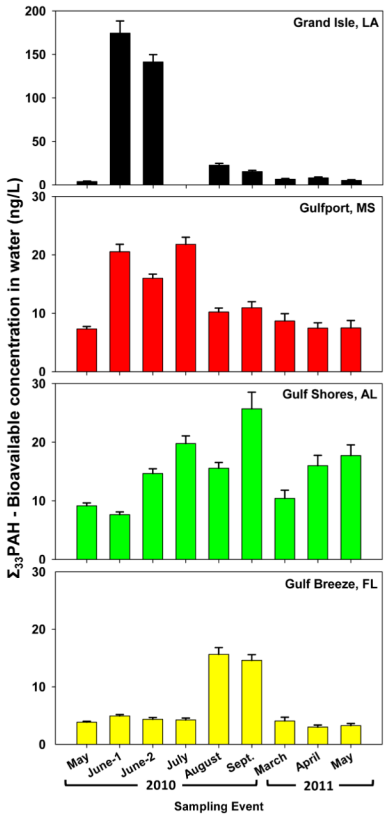

Figure 2. Bioavailable concentration of PAHs in coastal waters of the Gulf of Mexico

Bars represent the dissolved concentration of the sum of 33 PAH compounds and error bars represent the calculated 95% confidence interval based on pooled variance from a replication study. Note that the scale is different for Grand Isle, LA. Exact sampling dates can be found in the methods.

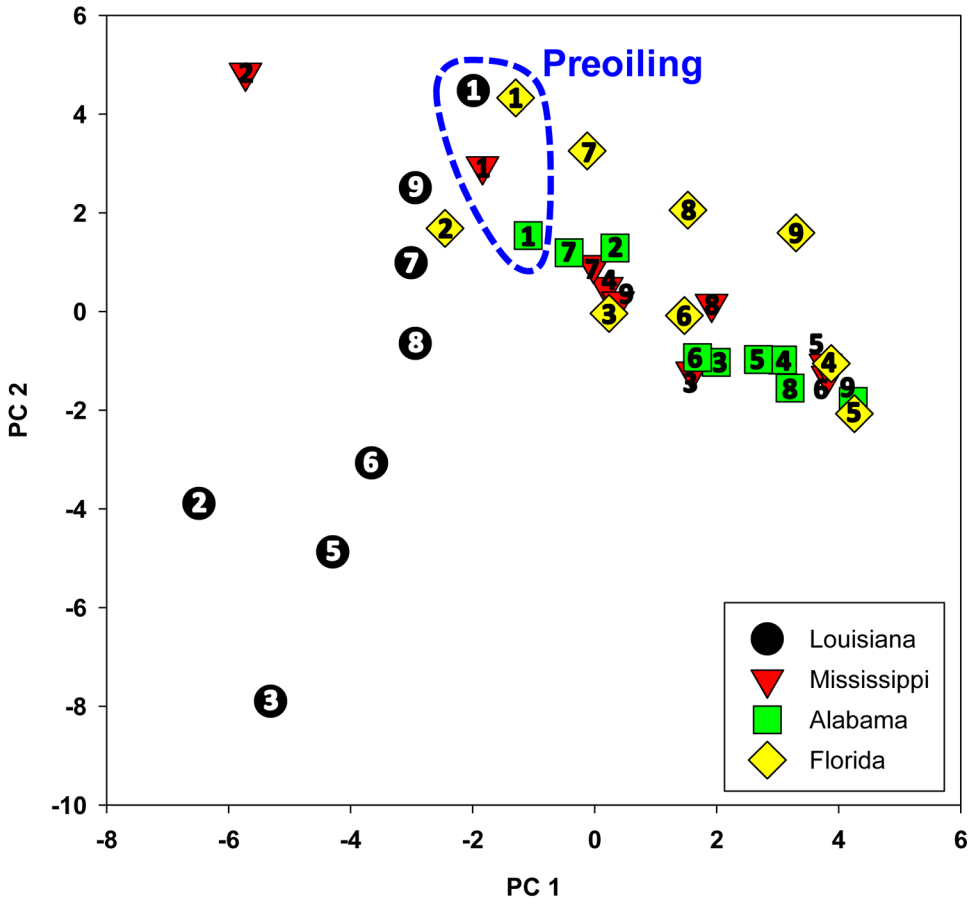

Figure 3. Principal components analysis of PAH chemical profiles

Principle component 1 and 2, together representing 49% of the variability in the data set, are plotted. States are differentiated by symbols and the numbers indicate the sampling events in chronological order. There is no month 4 sample for Louisiana. Data from samples taken during month 1, prior to shoreline oiling, are enclosed by a dotted line labeled “Preoiling”.