



# Distributions and accumulation rates of polycyclic aromatic hydrocarbons in the northern Gulf of Mexico sediments<sup>☆</sup>



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## ABSTRACT

Sediment samples collected from shelf, slope and interior basin of the northern Gulf of Mexico during 2011–2013, 1–3 years after the *Deepwater Horizon* (DWH) oil spill, were utilized to characterize PAH pollution history, in this region. Results indicate that the concentrations of surface  $\Sigma\text{PAH}_{43}$  and their accumulation rates vary between 44 and 160 ng g<sup>-1</sup> and 6–55 ng cm<sup>-2</sup> y<sup>-1</sup>, respectively.  $\Sigma\text{PAH}_{43}$  concentration profiles, accumulation rates and  $\Delta^{14}\text{C}$  values are significantly altered only for the sediments in the immediate vicinity of the DWH wellhead. This shows that the impact of DWH oil input on deep-sea sediments was generally limited to the area close to the spill site. Further, the PAHs source diagnostic analyses suggest a noticeable change in PAHs composition from higher to lower molecular weight dominance which reflects a change in source of PAHs in the past three years, back to the background composition. Results indicate low to moderate levels of PAH pollution in this region at present, which are unlikely to cause adverse effects on benthic communities.

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## 1. Introduction

The northern Gulf of Mexico (NGOM) has become one of the most extensively studied semi-enclosed seas in the world since the Deepwater Horizon (DWH) oil spill in 2010. On an annual scale this region receives a large amount of hydrocarbons, including potentially toxic polycyclic aromatic hydrocarbons (PAHs) from a variety of sources e.g. Mississippi River discharge, coastal erosion, atmospheric deposition, natural oil seeps, gas hydrates and accidental oil leaks related to petroleum exploration/transportation (Mitra and Bianchi, 2003; Overton et al., 2004; Wade et al., 1989). In addition to these background sources, the DWH oil spill released  $\sim 2.1 \times 10^{10}$  g of PAHs into the NGOM waters (Reddy et al., 2012). PAHs with relatively low aqueous solubility get readily sorbed onto soil and sediments, and eventually deposited to the seafloor

(Adhikari et al., 2015; Dachs et al., 2002; Lipiatou et al., 1997; May et al., 1978). The seafloor sediments are considered to be the long term repository of PAHs and the deep-sea sediments are therefore the major global sink for PAHs entering into ocean waters (Gustafsson et al., 1997).

It has been estimated that 0.5–31% of the oil, with ~4% of associated PAHs, released during DWH oil spill may have been deposited in 3200–8400 km<sup>2</sup> of the NGOM seafloor (Chanton et al., 2015; Reddy et al., 2012; Valentine et al., 2014). These estimates are based on utilization of chemical biomarkers (hopanes; Valentine et al., 2014) and isotopic tracers (<sup>14</sup>C; Chanton et al., 2015) to detect oil contamination in the seafloor sediments. Whereas biomarker compounds like PAHs have relatively low concentrations in oil (Neff, 1979) and do degrade through time (Cerniglia, 1992; Hinga et al., 1980; Neff, 1979), they have been used in detecting oil pollution in the environment due to their relatively longer persistence than aliphatic compounds (Alimi et al., 2003; Wang et al., 1999) over at least decadal time scales (White et al., 2005; Short et al., 2007). The use of <sup>14</sup>C as an “inverse” isotopic tracer (oil is devoid of <sup>14</sup>C, which has a half-life of 5760 y) has been well-established in oil pollution studies (Chanton et al., 2012, 2015;

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Cherrier et al., 2014; Pendergraft et al., 2013; Pendergraft and Rosenheim, 2014; Reddy et al., 2002; Slater et al., 2005; White et al., 2008). Combination of both biomarker and isotopic tracers of petroleum pollution to the environment can add inference about processes that may transform the oil into compounds with less volatility and longer residence time in the sediment (Aeppli et al., 2012, 2014; Pendergraft and Rosenheim, 2014).

The seafloor deposition of an unprecedented amount of PAHs can substantially increase their concentrations in sediments and impair the benthic communities. The toxic, carcinogenic, mutagenic and persistent nature of PAHs (Albers, 2003; Samanta et al., 2002) coupled with the large fishing industry in the Gulf make them a critical group of organic contaminants that need to be monitored thoroughly. There are few pre (Brooks et al., 1986; Overton et al., 2004) and post (Turner et al., 2014; Wang et al., 2014) DWH oil spill studies on sediment PAHs in the shallow coastal regions of the GOM however, similar studies from the deep-sea of the NGOM are not available. In general PAHs are considered to be persistent in nature however, various diagenetic processes acting on deposited PAHs can alter their initial concentrations (Berrojalbiz et al., 2011; Gutierrez, 2011; Head et al., 2006). Thus, it is important to monitor the DWH-related influx of PAHs into the sediment in order to determine their long term fate and impact on benthic organisms. In the present study, we collected post DWH oil spill sediment samples from various regions of the NGOM and compared their PAHs composition with the publicly available values in the samples collected immediately after the spill from the same areas of the NGOM (<http://www.gulfspillrestoration.noaa.gov/oil-spill/gulf-spill-data>, reported by the Natural Resource Damage Assessment, NRDA) in order to understand the long term fate and distribution of PAH compounds in the sediment. The focus of this study is to characterize post-spill (1–3 years after the DWH oil spill) PAH pollution in selected NGOM shelf, slope and deep-sea sediments in-terms of their concentrations, compositions and accumulation rates and compare them with sediment deposited before the spill occurred.

## 2. Materials and methods

### 2.1. Sample collection

Sediment cores were collected from 17 sampling stations (Fig. 1) on board three different cruises in 2011 and 2013, in the NGOM. Sediment samples from sites C1–C8 were collected aboard *R/V Endeavor* in August 2011, cores C9–C11 were collected aboard the *R/V Walton Smith* in April 2013, while cores C12–C17 were collected from the *R/V Pelican* in June 2013. The sampling stations C1–C7 represent shallow coastal stations, C9–C13 as deep-sea stations east of Mississippi River (MR) delta in the vicinity of the DWH oil spill site, and the rest (C8, C14–C17) represent deep-sea stations west of the MR delta (Fig. 1). Sediment cores were collected using a low-bow wake multi-corer (Ocean Instruments, Inc. MC-800) with eight collection tubes. Two undisturbed cores from each cast were chosen for PAHs and  $^{210}\text{Pb}$ -dating for this study. Only the top 6 cm of one core from each station were analyzed for PAHs whereas the entire second core was used for  $^{210}\text{Pb}$ -dating. Sediment cores for PAHs analysis, collected in 2011 were sectioned into 2 cm intervals while the cores collected in 2013 were sectioned at 1 cm intervals up to 2 cm and at 2 cm intervals thereafter. The only exceptions were station C9 and C10, in the vicinity of DWH which were sliced at 0.5 cm intervals up to 2 cm, at 1 cm intervals for next 2 slices and into 2 cm thereafter. The sediment subsamples for PAHs analysis were frozen at  $-20\text{ }^\circ\text{C}$  until further lab processing. Sediment cores collected for  $^{210}\text{Pb}$ -dating were sliced at similar intervals and directly collected in graduated glass vials and stored until analysis.

Sediment samples from a single NE–SW transect in 2013 were subsampled for  $^{14}\text{C}$  analysis – starting near the DWH wellhead (C12) and going progressively south west (C13 and C17). The samples for radiocarbon analysis, were subsampled at 0.5 cm resolution for the first 2 cm, and then 1 cm resolution to 5 cm with metal spatula and transferred immediately to pre-combusted glass vials with pre-combusted ( $525\text{ }^\circ\text{C}$ , 2 h) aluminum foil (Pendergraft et al., 2013; Rosenheim et al., 2008).

### 2.2. PAHs extraction and analysis by GC/MS

The sediment PAHs were extracted using EPA SW-846 method 3540C (US EPA, 2000). Prior to extraction, the frozen samples were transferred to refrigerator until defrosted and then homogenized by vigorous stirring. Subsamples of  $\sim 30\text{ g}$  of sediments were taken into a pre-cleaned 500-ml beaker, spiked with surrogate recovery standard (phenanthrene-d10) and mixed with pre-cleaned anhydrous sodium sulfate until a dry sand-like matrix was created and transferred into a Soxhlet extraction thimble. Then the samples were Soxhlet-extracted for 24 h with dichloromethane (DCM). The solvent extracts were then concentrated by rotary evaporation and nitrogen blowdown to 1 ml. Just prior to the analysis by GC–MS, a mixture of internal standards composed of naphthalene-d8, acenaphthene-d10, chrysene-d12, and perylene-d12 was added to the final sample extracts. The details on sample analysis using GC/MS and quality assurance/quality control (QA/QC) are explained elsewhere (Adhikari et al., 2015). Briefly, the sample extracts were analyzed using an Agilent 7890A GC interfaced with an Agilent 5975C inert XL mass selective detector (MSD) operated in the selective ion monitoring (SIM) mode targeting for 43 PAHs; 18 parent PAHs with 2–6 aromatic rings (naphthalene to Benzo[*g,h,i*]perylene) and 25 alkyl-substituted homologues of the parent PAHs. One procedural blank for 15 samples was processed and analyzed in the same manner as the real samples. The concentrations of target analytes in the blanks were below detection to  $<2\%$  of their concentrations in real samples. The surrogate recoveries varied between 53 and 125% ( $67.0 \pm 10.0\%$ ). Reported concentrations of target analytes are recovery-corrected. The concentrations were normalized to dry weights of the sediments, and the sum of all 43 individual PAHs is presented as  $\sum\text{PAH}_{43}$ . A list of 43 PAH compounds identified and quantified in this study is presented in Supplemental Document.

### 2.3. $^{210}\text{Pb}$ analysis using gamma spectroscopy

Aliquots of finely ground dry sediments (8–30 g) were placed into counting vials of known geometry, sealed and measured for  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  (via  $^{214}\text{Pb}$ ) by direct gamma counting using high-purity germanium well detectors (Maiti et al., 2010; Yeager et al., 2004). All activities were corrected for decay to the midpoint of sample collection. Measurement of  $^{210}\text{Pb}$  was based on its emission at 46.5 keV and  $^{226}\text{Ra}$  by the 351 keV emission of its daughter isotope  $^{214}\text{Pb}$ . Unsupported  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ) was calculated as the difference between the measured total  $^{210}\text{Pb}$  at 46.5 keV and the estimate of the supported  $^{210}\text{Pb}$  activity given by its parent nuclide at 351 keV [ $^{210}\text{Pb}_{\text{ex}} = ^{210}\text{Pb}_{\text{tot}} - ^{214}\text{Pb}$ ]. The  $^{210}\text{Pb}_{\text{ex}}$  profiles were used to calculate sedimentation rates from surface to the deepest layer, where excess activities were detected. Below these layers the  $^{210}\text{Pb}_{\text{ex}}$  activities were  $\leq 0$ , within the propagated error. Errors represent counting statistics.

### 2.4. $^{210}\text{Pb}$ modeling approach

Linear sedimentation rates ( $\text{cm yr}^{-1}$ ) and sediment accumulation rates ( $\text{g cm}^{-2}\text{ yr}^{-1}$ ) were calculated using CRS (constant rate of

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