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Vertical fluxes of polycyclic aromatic hydrocarbons in the northern Gulf of Mexico

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) concentrations in dissolved, suspended and sinking phases were measured in the northern Gulf of Mexico during 2012 and 2013 to estimate rate of loss of particulate PAHs from the water column via sinking fluxes. The concentrations of suspended particulate ΣPAH_{43} varied between 0.29–0.72 ng/L in 2012 and 0.17–1.31 ng/L in 2013 while dissolved ΣPAH_{43} varied between 31.2–51.2 ng/L and 24.2–58.0 ng/L in 2012 and 2013, respectively. The concentrations of dissolved PAHs were found to be orders of magnitude lower than the values reported during DWH oil spill. Sediment trap-based vertical sinking fluxes of particulate ΣPAH_{43} varied between 2.21–7.78 μg m^{-2} day^{-1} in 2012 and 1.95–2.53 μg m^{-2} day^{-1} in 2013. The vertical fluxes are found to be an important loss term for particle bound PAHs in this region with 3.1–6.7% of total particulate PAH inventory in the euphotic zone being lost daily via this pathway. The reported variability in the sinking rates of particle bound PAHs from the upper ocean can impact the residence time of PAHs in the upper ocean.

1. Introduction

Petroleum-derived hydrocarbons can be introduced into the marine environment via oil seeps/spills, riverine discharges, continental runoff, coastal erosion, and atmospheric deposition (Albers, 2003; Dachs et al., 2002; Lipiatou et al., 1997; Mitra and Bianchi, 2003; Park et al., 2001, 2002; Tsapakis et al., 2006). Among these hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) are of major environmental concern as some of the PAHs and their metabolic products are toxic, mutagenic and/or carcinogenic (Samanta et al., 2002; Yan et al., 2004). These hydrocarbons are readily taken up by plant and animal tissues, bioaccumulated in marine organisms and persistent in nature (Albers, 2003; Sverdrup et al., 2002; Tao et al., 2009). In general, PAHs have low aqueous solubility, with both solubility and volatility decreasing with increasing molecular weight (Albers, 2003; Mackay and Shiu, 1977; May et al., 1978). Due to their low solubility and high partition coefficients, PAHs entering into an aquatic environment get readily sorbed onto particles, mainly organic rich particulate matter (Dachs et al., 2002; Gustafsson et al., 1997a, 1997b, 2001; Ko et al., 2003; May et al., 1978). PAHs sorbed onto these particles in the open oceans are subsequently deposited to the sediments via vertical sinking which serves as a major mechanism for the removal and global cycling of particle reactive organic pollutants such as PAHs (Dachs et al., 2002; Lipiatou et al., 1997). The open ocean and the deep sea sediments are thus considered the major global sink for environmental releases of petroleum-derived hydrocarbons, and marine particles are thought to play a crucial role in the distribution, transport and fate of these hydrocarbons entering into ocean waters (Gustafsson et al., 1997a; NRC, 2003). However, other loss terms besides vertical sinking such as evaporation, biodegradation, photo-oxidation, dispersion, and lateral transport can also play an important role in PAHs dynamics in marine waters (Berrojalbiz et al., 2011). Researchers have long recognized the importance of quantifying vertical fluxes of such organic contaminants from surface to deep ocean in order to understand their dispersal and residence time in marine environment and construct global mass-balance fate models (Dachs et al., 1996; Lipiatou et al., 1993). Studies carried out during the last two decades have shown that large, rapidly sinking particles can account for a significant portion of the total flux of organic contaminants (Dachs et al., 1996; Elder and Fowler, 1977) and direct measurements of such particle-associated contaminant fluxes can be carried out using sediment traps (Bouloubassi et al., 2006; Dachs et al., 1996; Deyme et al., 2011; Lipiatou et al., 1993; Raoux et al., 1999; Tsapakis et al., 2006).

The northern Gulf of Mexico (GOM) provides an ideal location to investigate the role of marine particles in modulating vertical PAH fluxes. This region receives hydrocarbons from many sources including spills/leaks (over 1500 oil spills reported per year), numerous natural seeps, atmospheric deposits, and riverine input (Mitra and Bianchi, 2003; Park et al., 2001, 2002; Wade et al., 1989). An estimated 2.1×10^{10} g of PAHs also entered into the northern GOM waters during the 2010 Deepwater Horizon (DWH) oil spill (Reddy et al., 2012). A number of

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studies have been conducted to assess PAHs distribution in the northern GOM but they mainly focus on surface sediments, dissolved PAHs, and their toxicity to aquatic organisms (Allan et al., 2012; Diercks et al., 2010; Mitra et al., 2012; Sammarco et al., 2013; Xia et al., 2012). However, to date none of these studies addresses the vertical fluxes of particulate phase PAHs associated with sinking particles in the GOM. The absence of flux measurements in the water column limits our understanding of the distribution, transport and fates of PAHs in this region.

The major objective of this study is to quantify the vertical fluxes of particulate PAHs for the first time in the upper mesopelagic zone of the northern GOM. The mesopelagic or the "twilight" zone located between the base of the euphotic zone and 1000 m, is the zone of highest particle and organic matter attenuation with depth, with particulate matter sinking through this zone in relative short time frame. The mesopelagic layer has been considered as the largest "heterotrophic digester" of the oceans (Benner, 2000) and accounts for 95% of the fish biomass in the ocean (Irigoien et al., 2014). The nature, transformation and remineralization of organic matter through the mesopelagic layer affects the quantity and stoichiometry of material delivered to the bathypelagic zone and thus plays a critical role in setting a limit on the amount of PAHs that can be transported to the deep sea and seafloor sediments.

2. Materials and methods

2.1. Sample collection

Three types of samples (water for dissolved PAHs, suspended particles for particulate PAHs and settling particles for sinking PAHs) were collected from the vicinity of the DWH well head in the northern GOM aboard the *R/V Walton Smith* during April 2012 and 2013 cruises. In order to determine any spatial variability in PAH concentrations and fluxes in this region, sampling was carried out at three different locations; near Deepwater Horizon spill site (DWH), north of DWH (NDWH), and south of DWH (SDWH). These locations were repeated again in 2013 to identify any trend in temporal variability. Sampling locations for 2012 are labeled as NDWH-12, DWH-12 and SDWH-12, while sampling locations for 2013 are NDWH-13, DWH-13 and SDWH-13 (Fig. 1). The stations are ~100 km from the mouth of Mississippi River and in water depths of 1200–2000 m.

2.2. Dissolved

At each sampling station, vertical profiles of water samples were collected from 0 to 1000 m using shipboard CTD sampling rosette. At each depth, 20 L of water samples were collected for the analysis of dissolved PAHs. Immediately after collection, water in the Niskin bottles was directly passed through pre-conditioned solid-phase extraction (SPE) disks with C-18 media (C.I. Agent® Storm-Water Solutions, WA, USA). The solid-phase extraction of PAHs on C-18 media has been previously used in a number of studies (Kiss et al., 1996; Kootstra et al., 1995; Marce and Borrull, 2000). Flow rates during filtrations were kept constant at about 50 ml min^{-1} using Masterflex Peristaltic Pumps (Cole-Parmer, IL, USA). After the completion of filtration, the SPE disks were stored at −20 °C until analysis. The PAH concentration extracted from these disks represents total water column PAH concentration. Given the expected low particle concentration in the open ocean, no additional pre-filters were added in line with the SPE disks. The particulate PAH concentration were found to represent ~1% of total PAH concentration (next section) which is well within the analytical errors of total PAH concentrations measurements and hence considered negligible. For the practical purpose, these concentrations therefore were considered as dissolved PAHs.

2.3. Particulates

Particulate PAH concentrations in the open ocean are very low (Dachs et al., 1997; Gustafsson et al., 1997a; Lipiatou et al., 1997) therefore it was essential to collect and filter large volumes of water samples in order to get concentrations well above the detection limits of the analytical instruments. Particle samples were collected by *in situ* filtration using battery-operated submersible pumps (McLane Research Laboratories, Inc., Falmouth, USA). The pump deployment consisted of a vertical array of four pumps at 100, 150, 250, and 350 m depths. Two such deployments were performed at each station, one immediately after the deployment of sediment traps and the other just before the recovery

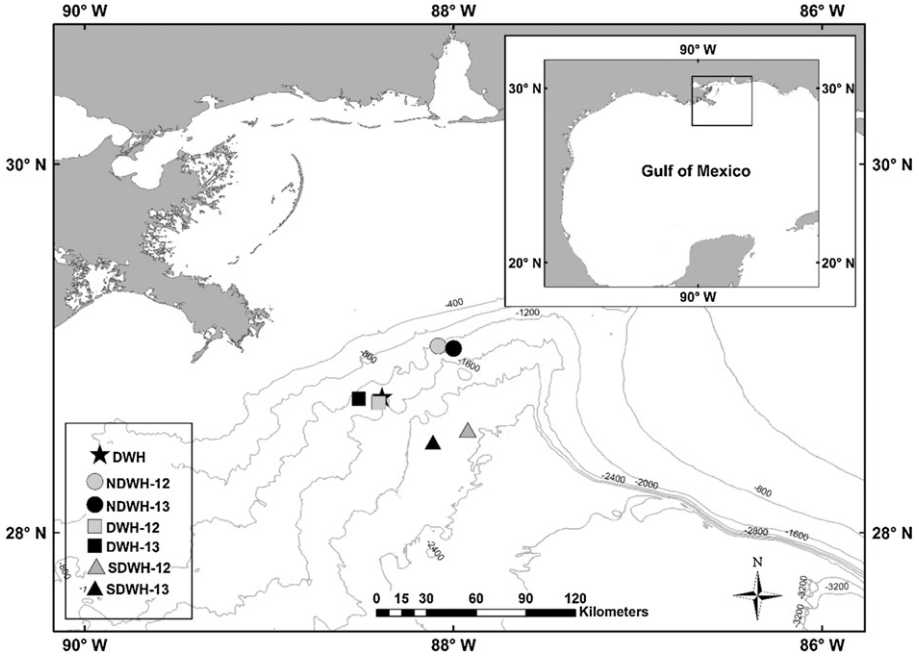

Fig. 1. Sampling locations in the northern Gulf of Mexico, in the vicinity of Deepwater Horizon (DWH) oil spill site. Sampling stations are, NDWH-12 and NDWH-13; north of DWH for 2012 and 2013, DWH-12 and DWH-13; at DWH for 2012 and 2013, and SDWH-12 and SDWH-13: south of DWH for 2012 and 2013.