



PAH and PCB body-burdens in epibenthic deep-sea invertebrates from the northern Gulf of Mexico

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ABSTRACT

There is a paucity of information on the levels of PAHs and PCBs in the deep-sea (≥ 200 m). In this study, the body-burdens of 16 PAHs and 29 PCBs were measured in: Actinaria (sea anemones), Holothuroidea (sea cucumber), Pennatulacea (sea pens), and Crinoidea (sea lilies) in the deep Gulf of Mexico. All epibenthic species were collected at depths of approximately 2000 m. The PAH and PCB congener profile displayed a similar pattern of bioaccumulation across all four taxa. The high molecular weight PAH, dibenz[*a,h*]anthracene, was the most abundant PAH in all organisms, ranging from 36 to 53% of sum total PAHs. PCBs 101 and 138 exhibited the highest levels at 20–25% of total congener concentrations in all taxa. The exposure to PAHs and PCBs is likely attributed to contaminated particulate organic matter that is consumed by the deposit and filter feeding epibenthic megafauna sampled in this study.

1. Introduction

The inundation of ecosystems by contaminants is widespread throughout both developed and remote locations around the world (Hylland, 2006; Santschi et al., 2001; Islam and Tanaka, 2004). In the Gulf of Mexico, hydrocarbon exploration and extraction, as well as various industrial activity along the coast has contributed to the pollution of many aquatic ecosystems by oil-derived (pyro and petrogenic) polycyclic aromatic hydrocarbons (PAHs) and ‘legacy’ industrial pollutants, such as polychlorinated biphenyls (PCBs) (Howell et al., 2008; Katner et al., 2010; Lakshmanan et al., 2010; Oziolor et al., 2018; Qian et al., 2001; Santschi et al., 2001; Willett et al., 1997). The propensity of both classes of compounds to bioaccumulate in organisms, biomagnify across food webs, and impart toxicity has led to environmental monitoring efforts to quantify their levels in various ecosystems (Biddinger and Gloss, 1984; El-Shahawi et al., 2010; Jensen et al., 1969; Livingstone, 1998; Nakata et al., 2003; Suedel et al., 1994).

PAHs in the marine environment mainly come from pyrogenic (combustion of organic matter) and petrogenic (petroleum-derived) sources (Hylland, 2006; Santos et al., 2017; Wolska et al., 2012). Low

molecular weight PAHs (LMWs, ≤ 3 aromatic rings) are volatile and easily degraded in the environment, while high molecular weight PAHs (HMWs, ≥ 4 aromatic rings) are more persistent and toxic (Budzinski et al., 1997; Wolska et al., 2012). Specifically, PAH metabolites can readily form DNA adducts (as is the case for benzo[*a*]pyrene) that can cause heritable DNA mutations, abnormal gene expressions, and contribute to widespread metabolic dysregulation and carcinogenesis (Cavalieri and Rogan, 1985; Moorthy et al., 2015).

In contrast, PCBs are ‘legacy’ persistent organic pollutants (POPs) and comprise a diverse family of compounds that possess 2–10 chlorine atoms distributed across two fused benzene rings (Safe et al., 1985). PCBs were originally used as dielectrics and coolants in electrical devices until they were banned in the late 1970s due to environmental concerns (Boyle and Highland, 1979). The environmental persistence and high bioaccumulation potential of PCBs results in their noticeable body-burdens in wildlife and humans (McFarland and Clarke, 1989; Tanabe et al., 1987). The exposure of wildlife and humans to PCBs is also implicated in a wider suite of subtle endocrine disorders, which include immunological, neurological and metabolic effects (Birnbaum, 1994; Crinnion, 2011; Oziolor et al., 2014).

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While attention is often focused on assessing PAH and PCB pollution in coastal/neritic ecosystems (Baumard et al., 1998a; Baumard et al., 1998b; Soclo et al., 2000; Qian et al., 2001; Monirith et al., 2003; Sánchez-Avila et al., 2012) very little is known of their distributions in the deep-sea. However, limited studies have shown the presence of PAHs and PCBs in organisms sampled from this remote region of the ocean. For example, Jamieson et al. (2017) quantified PCBs in amphipods from two deep-sea trenches (Kermadec and Mariana) at depths >10,000 m. Studies by Froescheis et al. (2000), and Mormede and Davies (2003) have detected higher levels of PCB body-burdens in various deep-sea fish relative to their surface-dwelling counterparts. Similarly, Soliman and Wade (2008) have detected higher levels of PAH body-burdens in deep-sea amphipods (sampled at 480 m depth) relative to shallow-water counterparts in the northern Gulf of Mexico (Soliman and Wade, 2008). Additionally, Unger et al. (2008) have shown that deep-sea cephalopods sampled from depths of 1000–2000 m in the western Atlantic Ocean widely accumulated PAHs and PCBs. These studies

highlight the deep-sea as a significant sink for PAHs and PCBs. The deep-sea benthic environments of the Gulf of Mexico also present themselves as being particularly vulnerable given the high level of commercial ship traffic, as well as oil and natural gas activities (Carr et al., 2011; Peterson et al., 2011; Allan et al., 2012; Steichen et al., 2012; White et al., 2012; Yin et al., 2015).

The present study measured the concentrations of 16 PAHs and 29 PCBs in epibenthic invertebrates sampled from a depth of ~2000 m on the continental slope in the northern Gulf of Mexico. This included specimens from Actinaria (sea anemones), Holothuroidea (sea cucumber), Pennatulacea (sea pens), and Crinoidea (sea lilies). As there is an overall paucity of information on PAH and PCB exposure of deep-sea invertebrate megafauna, there is need to investigate the body-burdens of these pollutants in deep-sea biota.

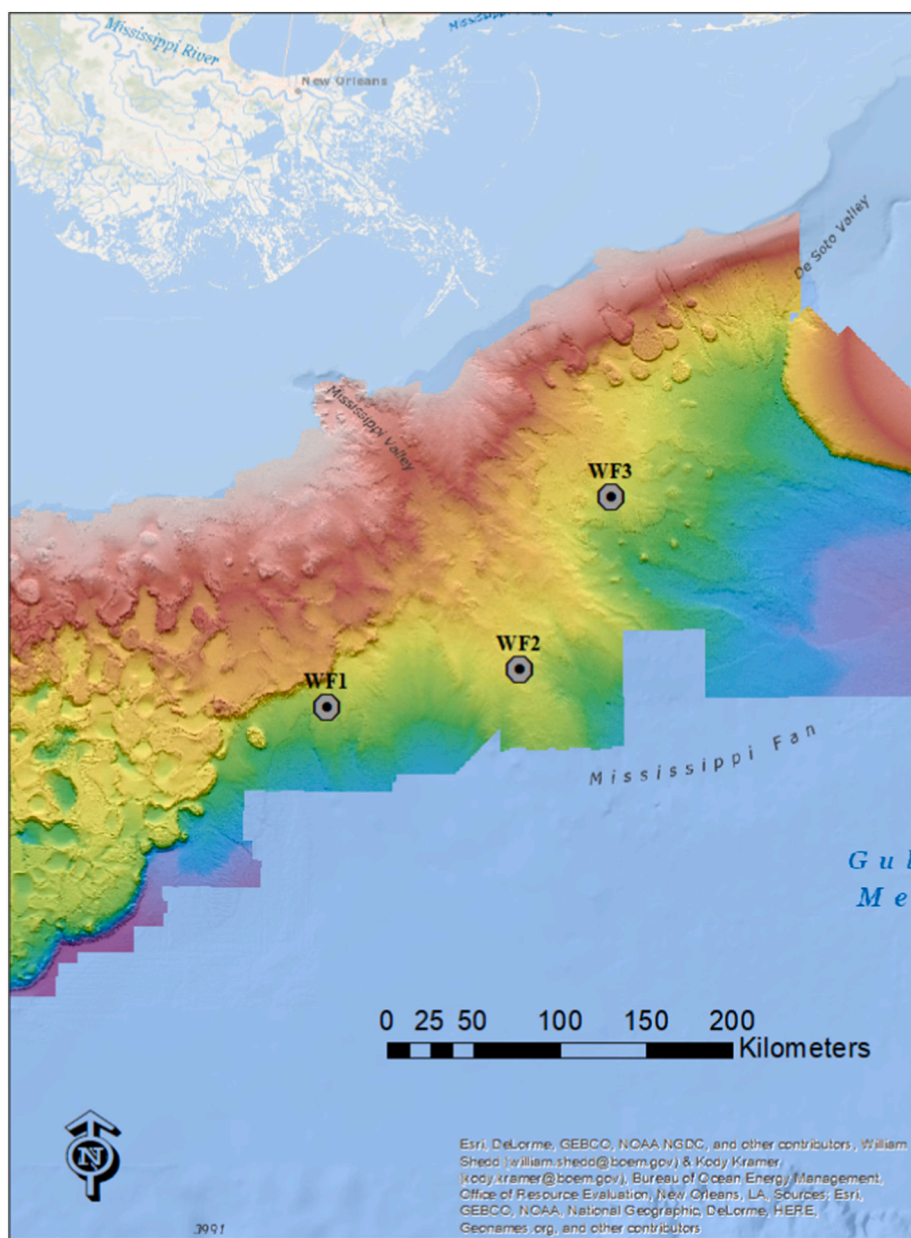


Fig. 1. The study area with marked sampling sites along the continental slope of the Mississippi Canyon in the northern Gulf of Mexico. Sampling sites were all at a depth of approximately 2000 m. Sites are labelled as WF to indicate the Wood Fall naming convention used during specimen collection.

2. Materials and methods

2.1. Sample collection

The samples were collected from May 25, 2017 to June 3, 2017 onboard the R/V Pelican (Louisiana Universities Marine Consortium). All samples were collected at three locations on the continental slope in the northern Gulf of Mexico. WF1 (27.135502°N, −89.927205°W) was located just off the northern portion of the Sigsbee Escarpment at a depth of 2170 m, WF2 (27.312393°N, −88.926911°W) on the Mississippi Fan at 2000 m, and WF3 (28.105893°N, −88.451494) which was to the northeast of the Mississippi fan at a depth of 1998 m (Fig. 1). The organisms were collected using a vacuum suction sampler attached to the robotically operated vehicle (ROV), Global Explorer. The organisms sampled included actinarians (sea anemones (*Actinoscyphia aurelia*), $n = 7$), holothuroideans (sea cucumber (*Benthodytes abyssicola*) (1), and *Benthodytes typica* (2)), $n = 3$), pennatulaceans (sea pens (*Kophobelemnon* sp.), $n = 2$), and an unidentified species of crinoid (sea lily, $n = 1$). Tissues were excised onboard, and all samples were immediately frozen at −20 °C until later processed for PAH and PCB quantification.

2.2. Sample extraction of PAHs and PCBs

Approximately 1 g of tissue (or entire organism if total mass available was <1 g) was used for analysis. Using this criteria, 1 g of tissue from the body wall of holothuroideans and 1 g of body wall and mesentery tissue from actinarians were sampled for the quantification of PAHs and PCBs, whereas whole-organisms were used for the pennatulaceans and the single crinoid. Samples were homogenized in 3 mL of 1:1 (v/v) hexane:ethyl acetate using a Bead Mill 4 Homogenizer (Fisher Scientific) operated at 300 g for 3–5 min. The homogenate was transferred to a 50 mL glass centrifuge tube and spiked with 5 µL of 100 µg mL^{−1} benzo[a]pyrene-d₁₂ (Sigma-Aldrich) and PCB 65-d₅ (CDN Isotopes) as internal standards (yielding a final concentration of 2.5 µg mL^{−1} in final volume). The homogenates were then sonicated in a Branson Ultrasonics™ M2800 Bath (Fisher Scientific) for 30 min. The glass tubes were then centrifuged for 10 min at 2000g. The resulting supernatant was removed and transferred to a pre-weighed 20 mL glass vial and then dried under a gentle stream of nitrogen (N₂). The vial was then weighed to record lipid weight of the sample. The lipid residue was reconstituted into 1 mL of acetonitrile (ACN) and transferred into a 2 mL glass amber vial and dried down using a Savant™ SPD121P SpeedVac™ Concentrator (Thermo Scientific). The resulting residue was reconstituted into 200 µL of ACN and transferred to a 200 µL glass insert. All samples were then stored at −20 °C for 1 h to precipitate lipids and other aqueous debris (Hong et al., 2004; Cullen et al., 2019). Following freezing, a 50 µL aliquot of the lipid-free supernatant was removed and transferred to a 2 mL glass amber vial. This aliquot was again dried using the Savant™ SPD121P SpeedVac™ Concentrator, reconstituted with 50 µL of dichloromethane (DCM), and transferred to a small-volume (100 µL) insert prior to gas chromatography–mass spectrometry (GC–MS) analysis. Background contamination was controlled by washing reusable glassware in a 5% Alconox™ detergent solution, and then transferring it to a 1% HCl_(aq) solution, followed by combustion at 500 °C for ~12 h.

2.3. GC–MS analysis of PAHs and PCBs

Standards for acenaphthene (ACE), acenaphthylene (ACY), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[g,h,i]perylene (BghiP), fluoranthene (FLT), pyrene (PYR), and PCBs 1, 18, 52, 101, 138, and 180 were acquired from Sigma-Aldrich. Anthracene (ANT), chrysene (CHR), benzo[a]anthracene (BaA), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DahA), fluorene (FLU), indeno[1,2,3-cd]pyrene (IcdP), phenanthrene (PHE), and naphthalene (NAP) were acquired from Supelco; and the compounds PCB 28, 33, 77, 81, 95, 105,

114, 118, 123, 126, 128, 149, 153, 156, 157, 167, 169, 170, 171, 177, 183, 187, and 189 from Ultra Scientific. All standards were of analytical grade.

All samples were quantified for 16 PAHs and 29 PCBs using a Hewlett Packard HP-6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC–MS). A splitless sample injection was performed at a volume of 2 µL. Chromatographic separation was performed using a 30 m × 0.25 mm DB-5MS capillary column with a 0.25 µm film thickness (J&W Scientific). Ultra-pure helium was used as the carrier gas with a flow rate of 1 mL min^{−1}. The GC front inlet and the MS interface were set to 250 °C and 280 °C, respectively. The GC oven was initially set at 40 °C, but following sample injection ramped up at a rate of 20 °C min^{−1} to 180 °C, and then at 5 °C min^{−1} until it reached 300 °C, where it was held for 10 min. The MS was run in electron impact ionization mode (EI) at an electron energy of 70 eV, and a source temperature of 230 °C. The 45 PAHs and PCBs were identified using selected ion monitoring (SIM).

Each compound was quantified against individual 13-point linear calibration curves ($R^2 > 0.97$), constructed using serially diluted reference standards (2.5–10,000 ng µL^{−1}). The limit of detection (LOD) was set to 5 times the background noise for the lowest detectable point on the calibration curve. Blanks were run before and after analysis to rule out possible contamination. Details on method optimization are presented elsewhere (Cullen et al., 2019). For brevity, matrix spike/recovery trials yielded an average % recovery of 95–100% for acenaphthene and benzo(a)pyrene, and 71–92% for PCBs 101 and 138.

2.4. Data analysis

Statistical analysis of PAH and PCB concentrations was performed on a ng g^{−1} wet weight (ww) basis to compare burdens of these pollutants across the different taxa. Differences in body-burdens based on geographic location were not tested since low and variable sample sizes at each location precluded this analysis. Differences in total burdens of PAHs and PCBs were tested in actinarians and holothuroideans by Mann-Whitney *U* tests due to low and unequal sample sizes; pennatulaceans and the crinoid were not included due to very low sample sizes. A permutational multivariate analysis of variance (PERMANOVA) using a Bray-Curtis dissimilarity matrix was performed only on actinarians and holothuroideans due to small sample sizes of pennatulaceans and the single crinoid. If significant differences were detected, pairwise comparisons with Bonferroni-adjusted *p*-values were calculated. Finally, multivariate analysis of congener concentrations via redundancy analysis (RDA) was performed on ln(*x*+1) transformed data where values that were not detected (ND) or below the limit of detection (<LOD) were represented as zero. RDA was conducted on transformed congener concentrations scaled to unit variance. The taxonomic group was used as the constraining variable for this analysis. All multivariate analyses (PERMANOVA and RDA) were conducted using the *vegan* package in R (v 2.5–2; Oksanen et al., 2018). All statistics conducted in R (R Core Team, 2018) with significance set at $\alpha = 0.05$.

3. Results

3.1. Body-burdens of PAHs and PCBs

The PAH and PCB body burdens were reported as ng g^{−1} ww and not as lipid normalized basis as (at maximum) the lipid fraction only comprised $6.19 \pm 1.21\%$ (mean ± standard error) of total biomass (Table 1). Furthermore, pairwise comparisons between actinarians and holothuroideans (two taxa with sufficient samples sizes for statistical testing) showed no significant differences in lipid weights (Welch's *t*-Test: $t = 1.21$, $df = 3.14$, $p = 0.31$). Statistical analysis of congener proportions relative to total PAHs or PCBs using PERMANOVA showed no statistically significant differences in pollutant body-burdens between actinarians (sea anemones) and holothuroideans (sea cucumbers) (pseudo- $F_{1,8} = 0.975$, $p = 0.385$). One PAH and 12 PCB congeners were

Table 1

Individual congener concentrations, as well as sum total concentrations for PAHs and PCBs in each taxa. All concentrations are listed as ng g⁻¹ (mean \pm standard error). Missing values are indicative of a concentration < LOD.

Compound	Actinaria (n = 7)	Holothuroidea (n = 3)	Pennatulacea (n = 2)	Crinoidea (n = 1)
PAHs				
Naphthalene (NAP)	122.02 \pm 50.80	88.11 \pm 51.78	240.98 \pm 5.76	195.50
Acenaphthylene (ACY)	123.09 \pm 51.74	77.66 \pm 60.15	248.97 \pm 7.26	203.91
Acenaphthene (ACE)	558.10 \pm 285.69	400.82 \pm 345.11	1713.12 \pm 698.22	748.91
Fluorene (FLU)	127.31 \pm 53.27	91.92 \pm 54.07	255.68 \pm 7.30	201.63
Phenanthrene (PHE)	130.91 \pm 54.62	93.38 \pm 54.72	308.38 \pm 47.18	211.29
Anthracene (ANT)	111.26 \pm 46.39	69.68 \pm 53.59	230.01 \pm 11.36	181.36
Fluoranthene (FLT)	134.79 \pm 56.22	98.15 \pm 57.99	1476.78 \pm 12.95	212.93
Pyrene (PYR)	119.00 \pm 49.69	86.16 \pm 50.60	237.14 \pm 5.97	198.05
Benzo[a]anthracene (BaA)	92.47 \pm 43.03	16.32 \pm 16.32	322.06 \pm 5.97	257.75
Chrysene (CHR)	65.61 \pm 30.46	11.58 \pm 11.58	228.61 \pm 4.31	174.36
Benzo[b]fluoranthene (BbF)	103.82 \pm 48.271	132.67 \pm 77.84	362.32 \pm 6.00	289.70
Benzo[k]fluoranthene (BkF)	124.51 \pm 52.11	89.70 \pm 52.42	248.86 \pm 5.90	197.27
Benzo[a]pyrene (BaP)	608.99 \pm 296.89	119.60 \pm 64.06	1931.45 \pm 536.57	1150.53
Indeno[1,2,3-cd]pyrene (IcdP)	284.53 \pm 110.80	195.00 \pm 114.37	543.89 \pm 10.49	428.43
Dibenz[a,h]anthracene (DahA)	1877.77 \pm 778.78	914.58 \pm 358.75	8169.67 \pm 45.61	5175.07
Benzo[g,h,i]perylene (BghiP)	56.18 \pm 28.68	32.54 \pm 32.54	656.87 \pm 14.01	–
Σ PAHs	4640.36 \pm 1910.34	2517.89 \pm 1332.75	17,174.78 \pm 1424.85	9826.68
PCBs				
Non-ortho				
PCB 77	56.18 \pm 30.00	10.95 \pm 10.95	216.89 \pm 4.44	164.33
PCB 81	53.29 \pm 28.53	10.39 \pm 10.39	205.58 \pm 4.15	155.75
PCB 126	84.76 \pm 41.13	108.24 \pm 66.70	323.56 \pm 23.44	228.09
PCB 169	115.45 \pm 48.08	83.76 \pm 48.82	239.20 \pm 1.67	186.36
Mono-ortho				
PCB 105	120.75 \pm 54.91	91.94 \pm 53.92	252.12 \pm 5.35	201.78
PCB 114	115.48 \pm 47.59	11.50 \pm 11.50	227.34 \pm 4.95	185.83
PCB 118	111.83 \pm 46.39	80.49 \pm 47.24	229.21 \pm 2.34	180.71
PCB 123	119.52 \pm 49.71	12.00 \pm 12.00	239.53 \pm 4.90	180.24
PCB 156	121.14 \pm 50.48	87.84 \pm 51.55	240.79 \pm 4.99	194.16
PCB 167	114.28 \pm 47.79	83.30 \pm 48.92	228.25 \pm 3.38	172.31
PCB 189	4.73 \pm 4.73	–	–	–
Non-dioxin-like				
PCB 1	94.05 \pm 39.30	68.06 \pm 39.99	189.03 \pm 4.45	149.01
PCB 18	132.85 \pm 66.42	77.51 \pm 45.28	226.24 \pm 5.88	167.26
PCB 28	–	–	226.54 \pm 7.20	–

Table 1 (continued)

Compound	Actinaria (n = 7)	Holothuroidea (n = 3)	Pennatulacea (n = 2)	Crinoidea (n = 1)
	9.97 \pm 6.44			
PCB 33	4.66 \pm 4.66	–	207.72 \pm 6.05	155.75
PCB 52	61.37 \pm 43.94	–	278.38 \pm 63.62	–
PCB 95	14.47 \pm 6.84	–	210.11 \pm 2.18	–
PCB 101	599.64 \pm 294.40	530.67 \pm 462.94	2160.81 \pm 757.87	1182.71
PCB 149	106.47 \pm 47.88	58.48 \pm 58.48	221.52 \pm 4.96	167.45
PCB 153	5.50 \pm 5.50	–	243.06 \pm 5.60	184.49
PCB 138	596.88 \pm 291.79	529.36 \pm 460.51	2174.79 \pm 668.69	1133.35
PCB 187	11.53 \pm 7.47	–	119.80 \pm 119.80	178.57
PCB 183	11.44 \pm 7.42	–	–	177.10
PCB 128	121.80 \pm 50.91	76.13 \pm 58.72	243.55 \pm 3.46	185.20
PCB 177	5.32 \pm 5.32	–	–	–
PCB 171	55.17 \pm 49.41	60.95 \pm 60.96	116.84 \pm 116.84	–
PCB 157	111.52 \pm 46.48	80.41 \pm 46.98	223.24 \pm 8.15	180.09
PCB 180	–	49.06 \pm 49.06	185.59 \pm 3.47	–
PCB 170	–	–	–	–
Σ PCBs	2955.32 \pm 1257.81	2111.04 \pm 1573.39	9429.70 \pm 1702.57	5710.53

removed from pairwise PERMANOVA comparisons between actinarians and holothuroideans, these included: chrysene (CHR) and PCBs 28, 33, 52, 95, 153, 187, 183, 177, 171, 180, 170 and 189. These congeners were removed from statistical analyses as they contributed <1% to total congener profiles.

Qualitative comparisons of normalized congener profiles to sum total PAH and PCB levels showed overall similar profiles for the pollutants across the four taxa (Fig. 2). For example, dibenz[a,h]anthracene (DahA) was measured in the greatest proportion among PAHs in all taxa, comprising ~47% of total PAHs. The highest levels for DahA were followed by benzo[a]pyrene (BaP) and acenaphthene (ACE) at ~11% and ~10% respectively (Fig. 2a). Similarly, normalized PCB congeners also showed overall similar profiles across all four taxa. The highest (and near equivalent) levels were observed for PCBs 101 and 138 at ~22% relative to total PCBs (Fig. 2b). Finally, significant differences between actinarians and holothuroideans were not detected for total PAH (Mann-Whitney *U* test, *W* = 13, *p* = 0.667) and PCB levels (Mann-Whitney *U* test, *W* = 16, *p* = 0.267) (Fig. 3).

3.1.1. Multivariate ordination analysis

RDA was used to look for characteristic associations of PAH and PCB body burdens explained by different deep-sea taxa (Fig. 4). Overall, the constraining variable (taxa) explained 39.42% of total variation and was determined to be significant following an ANOVA-like permutation test (on 1000 permutations; pseudo-*F*_{3,9} = 1.95, *p* = 0.038). Following a pairwise permutational test with Bonferroni-adjusted *p* values (1000 permutations), no significant differences were detected (*p* > 0.05). As RDA 1 explains 30.76% of the variance, the spread of taxa along this axis suggests that pennatulaceans have higher individual congener concentrations relative to all other taxa (actinarians and holothuroideans). The position of the single crinoid sample indicates relatively high concentrations relative to actinarians and holothuroideans, however due to a single sample, this observation requires further verification.

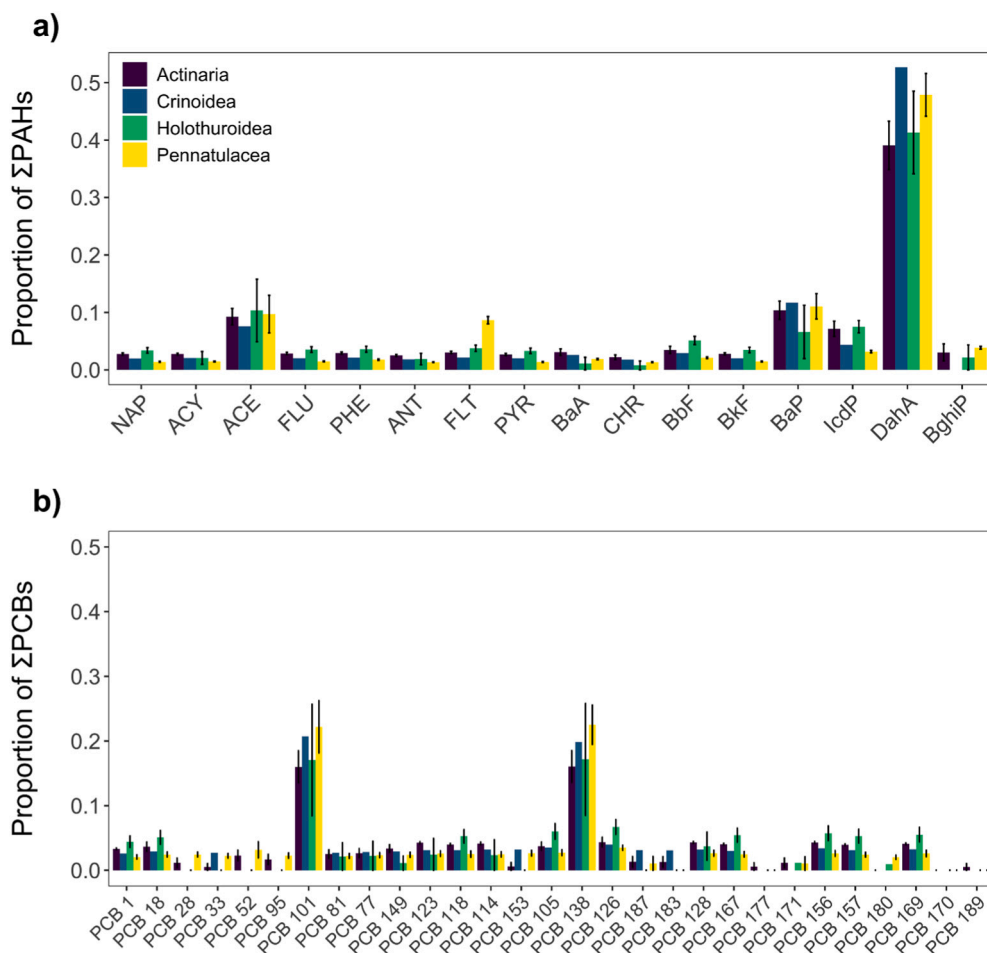


Fig. 2. Individual congener profiles across the four deep-sea taxa normalized to ΣPAHs (a) and ΣPCBs (b) respectively (shown as mean values \pm standard error).

4. Discussion

4.1. PAH body-burdens

The distribution of congener profiles of PAH body-burdens were similar across all four taxa (Figs. 2a, 3a). However, the sum total amounts of PAHs varied by almost an order of magnitude between the groups, with Pennatulacea exhibiting the highest levels at $17,174.78 \pm 1424.85 \text{ ng g}^{-1}$ (mean \pm standard error) ww, vs. $2517.89 \pm 1332.75 \text{ ng g}^{-1}$ ww in Holothuroidea. The HMW PAHs comprising DahA, and BaP (5 rings for each congener) accounted for the highest bioaccumulation in all taxa (5–53% of ΣPAHs). Additionally, the LMW PAH (i.e. 3 rings) ACE was also high across all four taxa (8–16% of ΣPAHs). The remaining congeners contributed only 1–5% of ΣPAHs individually (Fig. 2a).

Concomitant with increasing ring numbers (and associated molecular weights) of PAHs, their hydrophobicity as represented by the logarithm of the octanol-water partition coefficient or $\log K_{ow}$, also increases. Such increasing hydrophobicity further favors the partitioning of PAHs into non-polar matrices, such as the organic carbon of particulate materials (Yang et al., 2011), and the lipid fraction of organisms (Bond et al., 1985; Meador et al., 1995). Owing to this lipophilicity, these compounds should have a high affinity towards sinking particulate organic matter (POM), phytoplankton, and other biota in the water column. Once the compounds have reached the deep-ocean, high hydrostatic pressure, lack of sunlight, cold temperatures, and low microbial activities can slow pollutant degradation rates, thus making the deep-sea benthos a likely long-term sink for pollutants (Ramirez-Llodra et al., 2011; Tansel et al., 2011; Marini and Frapiccini, 2013).

All of the organisms analyzed in this study are detritivores, feeding on POM, also known as marine snow; the two feeding modes being suspension feeding (actinarians, pennatulaceans, and the crinoid), and deposit feeding (holothuroideans) (Macurda Jr. and Meyer, 1974; Roberts et al., 2000; Ammons and Daly, 2008; Williams, 2011). A possible mechanism that could transport these compounds to the deep-ocean is the biological pump, and downward flux of organic material to the seafloor, therefore, resulting in their incorporation into the benthic food web (Fowler and Knauer, 1986; Bouloubassi et al., 2006). Additionally, the affinity of PAHs towards the lipid fraction of organisms is a cause for concern as it enables bioaccumulation, ultimately attaining levels that may exhibit toxicity (Meador et al., 1995; Hylland, 2006).

PAH body-burdens in organisms comprising different trophic levels show some evidence of ‘trophic dilution’ where PAH concentrations decrease up the food chain (Wan et al., 2007). Such trends are evident when comparing between invertebrate (occupying lower trophic positions) and vertebrate species (occupying higher trophic positions) (Porte and Albaiges, 1994; Nakata et al., 2003), as well as within species that feed at multiple trophic levels (Gewurtz et al., 2000). Comparisons of the hepatic metabolism of BaP in rat vs. piscine species (mullet, *Mugil cephalus*) shows up to an order of magnitude higher activity in the mammal (for the formation of a diol metabolite) (Tan and Melius, 1986). Similarly, the metabolism of BaP has been shown to be $\sim 3\times$ faster in rats vs. fish (starry flounder (*Platichthys stellatus*) and English sole (*Parophrys vetulus*)) (Varanasi et al., 1986). Similarly, $\sim 3\times$ higher metabolism for BaP is evident in a piscine species (eels, *Anguilla anguilla*) vs. invertebrate (mussel, *Mytilus galloprovincialis*) (Machella et al., 2005). Therefore, higher ΣPAH levels are more commonly detected at lower trophic levels (which can mainly comprise invertebrate species), relative to

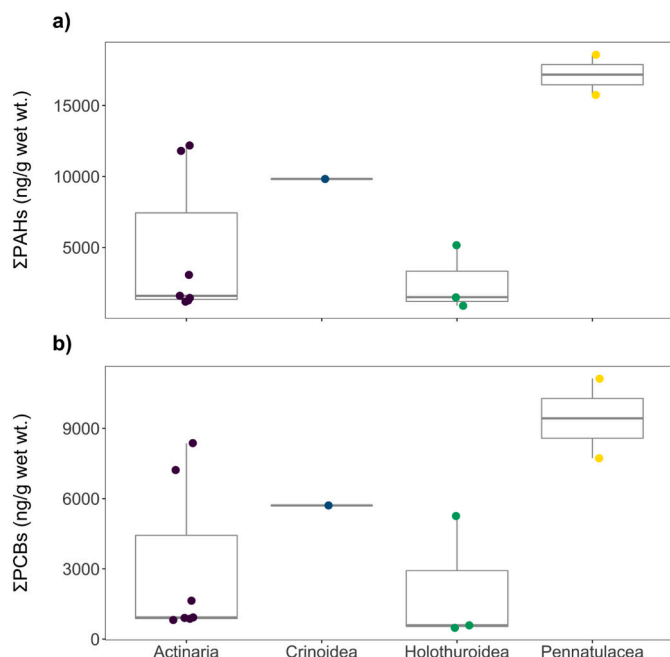


Fig. 3. Sum total concentrations or Σ PAHs (a) and Σ PCBs (b) across the four taxa of epibenthic invertebrate megafauna. Non-parametric statistical analysis (Mann-Whitney U test) was performed to only compare Actinaria and Holothuroidea due to a low sample size for the other taxa. No significant differences were observed. Points have been jittered (horizontally) to distinguish among points that would otherwise overlap.

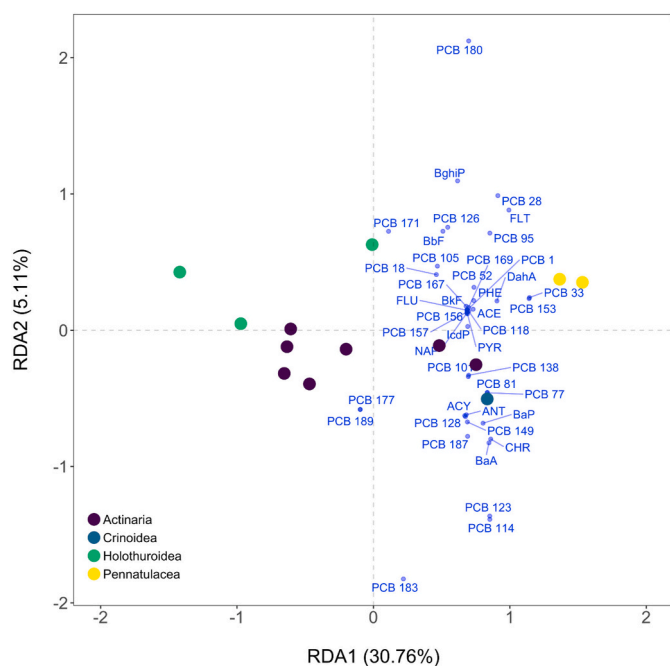


Fig. 4. Constrained multivariate analysis of congener concentrations via redundancy analysis (RDA) for PAH and PCB body-burdens in each of the four taxa. Refer to Table 1 for PAH abbreviations.

higher ones (mainly comprising vertebrate species) (Porte and Albaiges, 1994; Nakata et al., 2003).

In the present study, the lipid content was $6.19 \pm 1.21\%$ (mean \pm standard error) of wet tissue weight. This level is starkly contrasted to the high lipid content of hepatic tissues in apex predators, such as sharks ($\sim 4\times$ higher, 51–63% of ww) from the GoM (Cullen et al., 2019).

Despite this marked difference in lipid levels, the average Σ PAHs for each taxa of deep-sea megafauna in this study ranged from 2518 to 17,175 ng g⁻¹ ww, which is $\sim 2\times$ to $\sim 8\times$ of those reported in sharks from the Gulf of Mexico (Cullen et al., 2019). However, the high end of this range is occupied by those taxa with low representation in terms of sample size. Removing the pennatulaceans ($n = 2$), and the crinoid ($n = 1$) brings the range for average Σ PAHs to 2518–4640 ng g⁻¹. Mesopelagic fishes in the GoM showed values of 4.3–5015 ng g⁻¹ ww over a decadal period; though the highest values were observed following the Deepwater Horizon (DWH) disaster, and mainly LMW PAHs were observed (Romero et al., 2018). Deep-sea cephalopods also sampled from the GoM, displayed mean levels of up to 29,000 ng g⁻¹ lipid weight (lw) in mantle tissues. The concentrations were shown to increase following the DWH incident, and up to the year 2016 (Romero et al., 2020). Neritic studies on benthic invertebrates in the Arctic, Mediterranean, and GoM also report lower levels than what are observed in the present study. Pooling some of these reports together, ranges of 14.7–32,928 ng g⁻¹ dry weight (dw) total PAHs are seen, with the majority (77.5%) being <1000 ng g⁻¹ (Baumard et al., 1998a; Baumard et al., 1998b; Qian et al., 2001; Harvey and Taylor, 2017; Szczybelski et al., 2019; Ma et al., 2020).

While the overall hydrophobicity assists with the sequestration of PAHs into lipids, their bioavailability is not necessarily a function of such increasing hydrophobicity. In some cases, an inverse relationship has been shown for PAH bioaccumulation when comparing PAH levels in biota relative to concentrations in the surrounding environment (water or sediment). Baumard et al. (1998b) measured the preferential bioaccumulation of the highly water soluble PAH phenanthrene (~ 1.3 mg L⁻¹, (Mackay and Shiu (1977)) relative to the poorly water soluble anthracene (~ 0.1 mg L⁻¹, (Mackay and Shiu (1977))), in various benthic invertebrates (shrimps, crabs) from polluted sites across the Mediterranean sea. Although the levels of phenanthrene and anthracene were relatively equivalent in the surrounding sediments, a preferential bioaccumulation of phenanthrene was observed (Baumard et al., 1998b).

Wade et al. (2008), and Adhikari et al. (2016) sampled sediments from the deep GoM and reported Σ PAH concentrations ranging from 35.1–1033 ng g⁻¹ dw (90% > 500 ng g⁻¹). The highest levels were found on the continental shelf, and in proximity to the head of the Mississippi Canyon, with both studies showing exceptionally similar results. Sediments taken closest to the sampling sites from the present study were found to be below 100 ng g⁻¹. Relatively low bioaccumulation factors (BAFs) for LMW (0.46 \times for ACE) and HMW PAHs (0.23 \times and 0.39 \times for BaP and DahA, respectively) in the ampeliscid amphipod *Ampelisca mississippiana* were reported by Soliman and Wade (2008). As a result, an almost 1:1 correspondence was observed between total ‘parent’ PAHs in sediments and biota (amphipods). It should also be noted that the lipid content of the amphipods was relatively similar (5–11% dw) to that measured in the organisms from the present study ($6.19 \pm 1.21\%$ (mean \pm standard error) ww).

In contrast to the observations of Soliman and Wade (2008), high Σ PAH levels in invertebrates can also be seen relative to sediment concentrations. For example, Szczybelski et al., 2019 measured PAH BAFs ranging from 8–9 \times in benthic invertebrates (bivalves and polychaete worms) relative to the highly polluted surrounding sediment. Therefore, we can posit a minimum BAF 1 \times (as per Soliman and Wade (2008)), and a maximum of 9 \times (Szczybelski et al. (2019)). Also given a close to maximal sediment concentration of PAHs in GoM sediments of ~ 1000 ng g⁻¹ dw (from Wade et al. (2008) and Adhikari et al. (2016)), we find that the sum total PAH levels measured in holothuroideans (2518 ng g⁻¹ ww) and actinarians (4640 ng g⁻¹ ww), are within the putative range of BAFs bracketed by Soliman and Wade (2008) and Szczybelski et al. (2019). However, exceptions are found for pennatulaceans (17,175 ng g⁻¹ ww) and crinoids (9827 ng g⁻¹ ww), which contain low and variable replication (i.e. $n = 2$ for pennatulaceans, and $n = 1$ for crinoids), and posits the high PAH levels measured in this study with the caveat that further studies are needed to more comprehensively

sample these organisms.

There is a contrast between the PAH congener profiles reported for the benthic invertebrates in the present study and those from other studies. For example, the high proportionality of DahA (47% \sum PAHs) reported in this study (measured in organisms sampled at bathyal depths ~2000 m), differs from congeners typically reported in benthic invertebrates from neritic studies (<200 m). Typically, PAH congener profiles in these shallow-water invertebrates have been shown to largely encompass the low to medium molecular weight PAHs (Baumard et al., 1998b; Soliman and Wade, 2008; Rose et al., 2012; León et al., 2013; Zhang et al., 2020). However, it has been shown that DahA is the most prevalent PAH congener within tissues of various piscine species (~30–70% \sum PAHs) sampled from sites high in petroleum-based pollution (El Deeb et al., 2007; Said and El Agroudy, 2007). It could be suggested that the values quantified in the present study may be a result of differences in physiology/pollutant biotransformation based on variances among taxa and/or dissimilarities between environments (e.g. hydrostatic pressure, temperature, food availability, proximity to sources of pollution). Subsequently, the concomitant measures of PAHs in sediments and associated biota can provide a clearer indication of exposure and bioaccumulation potential, and constitutes an avenue for further work.

4.2. PCB body-burdens

The analysis of PCB body-burdens across the four taxa showed overall similar levels for the 29 measured congeners (Figs. 2b, 3b). However, PCBs 101 and 138 exhibited the highest levels at 20–25% of total congener concentrations. Whereas, contributions of the remaining congeners ranged from 1 to 4% of total congener concentration (Fig. 2b).

While PAHs can be of both anthropogenic (i.e., petrogenic spills and pyrolysis of hydrocarbons and or organic matter) and natural origins (i.e., forest fires, oil seeps), PCBs are exclusively of anthropogenic origin. The largest anthropogenic use of PCBs is associated with the electrical industry where they are used as heat absorbing and electrical insulating materials in transformers and capacitors (Delzell et al., 1994). Other minor sources also include from chlorination processes involved with pulp and paper mill industries (EPA, 1977). PCBs are discharged into the aquatic environment with effluents (such as for pulp and paper mills), or as a result of leakages of transformer or capacitor oils (Wolska et al., 2012). Furthermore, unlike PAHs, PCBs have the propensity to bio-magnify in higher trophic levels with carnivorous fishes exhibiting higher sum total PCB body-burdens relative to mostly invertebrate detritivores or filter feeders (Porte and Albaiges, 1994; Nakata et al., 2003).

Despite their known persistence and toxicity (McFarland and Clarke, 1989), the environmental degradation of PCBs favors de-chlorination of highly chlorinated congeners to low chlorinated congeners (\leq tetrachloro-PCBs) (Tiedje et al., 1993; Abramowicz, 1995). As a result, tri- and tetrachlorobiphenyls are among the most abundant PCB congeners measured in sediments from various sites in the GoM (Sant-schi et al., 2001; Mohrher et al., 2012; Oziolor et al., 2018). However, a detailed PCB congener profile quantified by NOAA in sediments from sites around Galveston Bay also showed a prominent presence of highly chlorinated PCBs, such as PCB 153 (six chlorines) and PCB 170 (seven chlorines) (NOAA, 2003). Despite these contrasting results in sediments, there is an overall lack of information on congener-specific bio-accumulation of PCBs in biota from the GoM. Our study is consistent with other studies on benthic invertebrates and fishes in that PCBs 138, and 101 are often found to be two of the most prevalent congeners present within biota (Voorspoels et al., 2004; Storelli et al., 2011; Zhang et al., 2013).

A direct comparison of PCB congener profiles measured in this study can be made with those measured by Cullen et al. (2019), who reported a predominance of highly chlorinated PCBs (PCB 153, PCB 138 (six chlorines), and PCB 187 (seven chlorines)) in three species of sharks

sampld from Galveston Bay and the northwestern GoM. This observation in fishes also agrees with studies from the North Atlantic and Northeast Pacific regions that show penta- and hexachlorobiphenyls, which included PCBs 101 and 138, to exhibit some of the highest concentrations relative to tri- and tetrachloro-PCBs (as measured in Atlantic cod, petrale sole, rockfish, Dover sole, etc.) (Froescheis et al., 2000). Of relevance to the present study, Jamieson et al. (2017) measured PCB levels in deep-sea amphipods sampled at depths of up to 10,250 m (Kermadec and Mariana trenches). The analysis of select PCB congener profiles showed PCBs 138 and 153 account for up to 65% of the total PCB concentration quantified in the amphipods, and the \sum PCB concentrations measured ranged from 18 to 382 ng g⁻¹ dw. The analysis of a wider range of 104 PCB congeners in deep-sea cephalopods sampled at depths of up to 2000 m in the western Atlantic exhibited quantifiable \sum PCB concentrations ranging from 0.8–278 ng g⁻¹ dw (Unger et al., 2008). Total PCB concentrations for neritic benthic invertebrates consolidated from several studies displayed a range from 0.84 to 24,000 ng g⁻¹ lw, (Voorspoels et al., 2004; Magnusson et al., 2006; Hong et al., 2011; Zhang et al., 2013). The average \sum PCB levels for each taxa reported in this study range from 2111 to 9429 ng g⁻¹ ww; but again, excluding the taxa with low sample sizes (pennatulaceans ($n = 2$), and the crinoid ($n = 1$)), average \sum PCB ranges fall to 2111–2955 ng g⁻¹. To our knowledge, these levels have not yet been reported in marine invertebrates, however, similar/higher levels have been found in some fresh water invertebrates (zebra mussel = 2929 ng g⁻¹ ww, amphipod = 4760 ng g⁻¹ ww) (Hanari et al., 2004).

Overall, there is a paucity of studies that concomitantly measure PCB levels in sediments and associated benthic fauna from deep-sea environments. More is known of near-shore or neritic environments. Studies by Willett et al. (1997), and Oziolor et al. (2018) show that levels of PCBs bioaccumulated in fish from various contaminated sites in Galveston Bay, which ranged by up to three orders of magnitude relative to levels measured in sediment. Another study found that BAFs between coral and sediments in the French Frigate Shoals were $\sim 1 \times$ (Miao et al., 2000). Magnusson et al. (2006) found that biota sediment accumulation factors (BSAFs) averaged between 0.5 \times and 6 \times , but could vary greatly within a species, and had no significant correlation to feeding strategy. At this time, it is unclear whether large BAFs/BSAFs are present for epibenthic invertebrate megafauna in the deep-sea, but if so, they would support high levels quantified in resident biota. Just as with PAHs, the monitoring of PCB levels will also be enhanced by concomitantly measuring sediment concentrations. The lipophilic nature of PCBs suggests an affinity towards the lipid fraction of organisms thus making adsorption to POM a likely mechanism for delivery to the deep sea. This is further supported by the fact that that downward particulate flux is a significant removal process of PCBs from the water column (Gustafsson et al., 1997). As previously described for the bioaccumulation of PAHs, all of the organisms in this study feed entirely or almost entirely on POM, suggesting it could be a major source in the bioaccumulation of PCBs as well.

5. Conclusion

This study reports on the levels of PAH and PCB congeners measured in four taxonomic groups of epibenthic deep-sea invertebrate megafauna collected off the continental slope in the northern Gulf of Mexico at depths ~2000 m. The megafauna included specimens from Actinaria (sea anemones), Holothuroidea (sea cucumbers), Pennatulacea (sea pens), and one from Crinoidea (sea lilies). Overall, comparable congener profiles of PAHs and PCBs was observed to bioaccumulate across all four taxa. The analysis of PAH levels indicated the presence of mainly HMW PAHs in these deep-sea invertebrates. Additionally, the analysis of PCBs showed a predominance of highly chlorinated penta- and hexachlorobiphenyls (PCBs 101 and 138, respectively). This observation agrees with the overall recalcitrant nature of highly chlorinated PCBs while also alluding to their high bioaccumulation potential. Our results

show that epibenthic deep-sea invertebrate megafauna are susceptible to PAH and PCB exposure. We surmise that the main delivery mechanism at play is contaminated particulate organic matter that is consumed by deposit and filter feeding organisms at the terminal end of the detrital food web. Future work should incorporate the measures of pollutant levels in the surrounding sediments and water column which the biota inhabit. In addition, the use of biomarker assessments for organismal health status (such as biotransformation enzyme activities) can also inform of possible negative health effects in exposed organisms.

CRedit authorship contribution statement

M. Chase Lawson: Conceptualization, Investigation, Writing - original draft. **Joshua A. Cullen:** Methodology, Formal analysis, Writing - review & editing, Visualization. **Clifton C. Nunnally:** Resources, Writing - review & editing, Visualization. **Gilbert T. Rowe:** Conceptualization, Resources, Writing - review & editing. **David N. Hala:** Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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