

**The distribution of polycyclic aromatic hydrocarbons in surface
sediments within the Mission-Aransas National Estuarine Research
Reserve, Texas**

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1. Introduction

The Mission-Aransas National Estuarine Research Reserve (NERR) is located 30 miles northeast of Corpus Christi, Texas. It includes about 200,000 acres of contiguous wetlands, terrestrial and marine environments, and is the third largest among the 27 NERRs in the nation. The Mission-Aransas NERR is productive and supports multi-million dollar sports and commercial fisheries, with an estimated value of \$260 million annually for commercial fisheries (NOAA Commerce Department). However, the productivity and health of this system are threatened by many human activities, such as oil and gas production, agricultural development, and urbanization.

Petrochemical industries are abundant within the Mission-Aransas NERR and around the city of Corpus Christi. To date, 649 oil and gas wells have been drilled in the NERR, and 40 of the wells still remain active (NERR Site Profile Document). Also, an existing network of pipelines transports oil and natural gas from wells to onshore refineries. In addition, all ship traffic, with a major fraction as oil tankers, enters the Port of Corpus Christi, the sixth largest port in the United States, through the Port Aransas Ship Channel, located just south of the Mission-Aransas NERR (Figure 1). The Port of Corpus Christi accepts around 70 million metric tons of petroleum each year (City of Corpus Christi data). Although much of the oil-gas production has been halted in the Mission-Aransas Estuary, recent drilling at deeper depths has been successful, making the continuation of large scale oil and gas production possible in this area (NERR Site Profile Document). Petroleum hydrocarbons can be potentially released to the surrounding aquatic environments during oil and gas production and transportation. The cumulative effects of these contaminant discharges are detrimental to the ecosystem (Kennish, 2002; U.S. Fish and Wildlife Service Ecological Services Corpus Christi, Texas, 1989).

Polycyclic aromatic hydrocarbons (PAHs) are one major component of petroleum, which can accumulate and persist in marine sediments (NOAA, 1988; 1991), and are mutagenic and carcinogenic. PAHs are also sourced from incomplete combustion of organic matter including natural fires and fossil fuels by cars and boats. PAHs can bioaccumulate in food chains, and thus eventually impact human health (Eisler, 1987; Kennish, 2002). The concentrations of PAHs in sediments have increased by several orders of magnitude in industrialized bays and estuaries during the past century, mainly due to the application and marine transportation of petroleum products (Herbes and schwall, 1978; Connor and Hugget, 1988). Many benthic organisms metabolize PAHs and accumulate intermediates (Livingstone, 1991; Varanasi, 1987). The PAH intermediates, which also can be mutagenic and/or carcinogenic, can bind to macromolecules, accumulate in organism tissues, and become available for trophic transfer to predators of benthic organisms (Driscoll et al., 1997; Leppanen and Kukkonen, 2000; McElroy and Sisson, 1989). Eventually, direct exposure to PAHs and their intermediates to human beings through consumption of sea foods can lead to problems with immunology and reproduction, and further cancers (ATSDR, 1995; Hawkins et al., 1998; Knaapen et al., 2004; Xia et al., 2004). In addition, growing evidence indicates that oxygenated PAHs (OPAHs), from photo-reactions and/or microbial degradation of PAHs, are potentially more mobile, bioavailable, and /or persistent than PAHs, and have important toxicological significance (Lundstedt et al., 2007). Some OPAHs and OPAH-containing fractions of environmental samples exhibited direct and higher toxicity to organisms and human cells (Xia et al., 2004). OPAHs in soil and air can be more concentrated than the USEPA priority PAHs, necessitating the need for further environmental characterization (Leotz-Gartziandia et al., 2000; Lundstedt et al., 2007).

Given the increased numbers of oil and gas wells and complex transportation pipelines within the Mission-Aransas NERR, concentration levels of PAHs in sediments of this marine system must be quantified to evaluate their ecological impacts. Unfortunately, no data are available for PAH concentrations in sediments in this NERR system. Indeed, a search using *ISI* Web of Science with keywords of “PAH+ Copano Bay/Aransas Bay” did not hit a single record. This study, therefore, is essential not only to assess the potential impacts of oil- and gas-wells on temporal and spatial concentrations of PAHs in surface sediments in the Mission-Aransas NERR, but also to provide baseline data for this region. Having this type of baseline information available will be critical to developing effective responses to future potential disasters such as the Deepwater Horizon oil spill, considering that many oil rigs are located in the shelf areas off the Mission-Aransas NERR in the Gulf of Mexico.

Our goal for this project is to fill the data gap concerning sources and distribution of PAHs within the Mission-Aransas NERR. Our long-term goal is to investigate temporal and spatial changes in concentrations of 16 USEPA priority PAHs (see below for the list) in the 5 time-series stations which have been continuously monitored in terms of water parameters by the Mission-Aransas NERR, and to decipher and quantify the contamination sources.

2. Materials and Methods

2.1. Sample collection

Sediments were collected on board R/V *C-Hawk* on March 10, 2011 by a home-made corer, with similar principles but a simpler version of the “HYPOX” corer (Gardner et al., 2009). Briefly, 15-cm sediment was taken at each sampling station, and the sediment cores were transferred to the lab immediately after the same-day cruise. The 15 cm sediment cores represent

approximately 30 years of sedimentation according to the sedimentation rates in this area (0.09-0.53g cm⁻² yr, Yeager et al., 2006). The sediment was sectioned at depth intervals of 0-5, 5-10, 10-15cm, and further freeze-dried in laboratory. Only the surface sediments (0-5 cm) were used for this study, thus the time scale investigated here should be within 10 years, considering the bioturbation in surface sediments.

2.2. PAH extraction and analysis

The extraction of sediment PAHs was based on the protocol of Rhind et al. (2009). Briefly, approximately 1g (dry weight) of sediment was extracted using ethanoic potassium hydroxide (1M) at 90°C for 8 h. Five deuterated PAHs (*D*₁₀- Acenaphthene, *D*₁₀- Fluorene, *D*₁₀- Phenanthrene, *D*₁₂- Benzo[*a*] anthracene, *D*₁₂- Benzo[*e*]pyrene) (sigma) were used as surrogate standards. The extracted PAHs were cleaned up with activated silica gel column. The column was packed with activated silica gel and topped with about 1cm anhydrous sodium sulfate. The samples in the column were eluted with dichloromethane/hexane (1:4, v/v). The eluted solution was concentrated and exchanged by hexane to 1 mL by a rotary evaporator, and stored in a freezer until further analysis.

PAHs were analyzed by gas chromatography–mass spectrometry (GC/MS, Shimadzu QP2010 plus), and 16 USEPA priority PAHs plus 2 alkylated PAHs were quantified: naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz(*ah*)anthracene, benzo[*ghi*]perylene, and indeno(1,2,3-*cd*)pyrene. The GC was equipped with a RXi-1MS capillary column (20 m×0.18 mm i.d., film thickness 0.18 μm), with helium as the carrier gas.

The oven temperature was hold at 60°C for 1 min, increased to 240°C at a rate of 10°C/min, and increased to 280°C at a rate of 4°C/min and hold 3 min. The temperatures of the injector and detector were 260°C and 275°C, respectively. The injection volume was 1 µl in a split mode (1/20). Method blanks were analyzed by the same procedure as the samples to determine any background contamination. The averaged surrogate recovery rates were 100±14%.

3. Results and Discussion

3.1. Concentrations of PAHs

The concentrations of total PAHs ranged from 102.7-195.4 ng g⁻¹ (dry weight sediment) in surface sediments of the 5 stations within the Mission-Aransas NERR (Table 1 and Fig. 2). Total PAH concentration in the Aransas Bay sediment was 195.4 ng g⁻¹, about 1.7 times higher than the mean value of the rest sediments (102.7-130.2 ng g⁻¹). The concentration levels at these stations are at the low end of contamination ranges found in estuaries and coasts. For example, total concentrations of PAHs in the sediments of the San Francisco Bay ranged from 40-6300 ng g⁻¹ (Pereira et al., 1999), and of the Boston Harbor ranged from 7,300 to 358,000 ng g⁻¹ (Wang et al., 2001). In a survey of the Corpus Christi Bay, it was reported that the concentrations of total PAHs in sediments ranged from 1.5 to 15.5 µg g⁻¹ in the North Bay and along the Tule Lake (shipping) Channel. Consistently, our data showed that the total concentration at one station (Station 51, Dunton et al., 2001) reached 19,400 µg g⁻¹ in the Nueces Delta (unpublished data). Overall, the concentration levels found in the Mission-Aransas NERR are much lower than the effects range low and/or effects median values (ERL/ERM) for the total PAHs in sediment (4022/44792 ng g⁻¹) compiled by Long et al. (1995), suggesting that there are no negative biological impacts due to PAHs in the areas surveyed in this study.

3.2. Composition of PAHs

The PAHs were dominated by naphthalene (2 rings) and phenanthrene (3 rings), accounting for 11-18% and 17-21% of the total, respectively (Fig. 3). The alkylated naphthalenes (1- and 2-methyl) on average represented 4.3% of the total PAHs. The dominance of 2-3 ring PAHs and the abundance of alkylated naphthalene are consistent with a commonly observed combustion or weathered petroleum source profile (Blumer and Youngblood, 1975). Acenaphthylene, fluoranthene, pyrene, and benzo[*b*]fluoranthene, with 3-5 rings, accounted for 8%, 9%, 8% and 6% of the total, respectively. The rest of the PAHs were all minor components, within 5% of the total.

From the overall composition the Aransas Bay sediments contained more abundance of PAHs with higher number of rings, such as pyrene and benzo[*b*]fluoranthene (Fig. 3). To further explore this pattern, we separate the 18 PAHs into 3 groups according to the number of rings within their structures: (a) with 2 rings including naphthalene, 1 or 2 methyl-naphthalene; (b) with 3-4 rings including acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, and chrysene; (c) with 5-6 rings including benzo[*b*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene. Structural information of PAHs can help distinguish between pyrogenic vs. petrogenic sources. The rationale for this separation is that petrogenic PAHs generally have more abundant of 2-3 rings, while pyrogenic PAHs contain more 4-6 rings (Bjoeseth 1985). Concentrations of the two-ring PAHs were similar, ranging from 23.7-35.7 ng g⁻¹, and there were no statistical differences among the 5 stations (Fig. 4a). However, concentrations of the 3-4 ring PAHs were 2-3 times higher in the Aransas Pass sediments than those in the rest sediments (Fig. 4b). The same pattern was observed for the PAHs with 5-6 rings (Fig. 4c).

Principal component analysis (PCA) is often used to distinguish compositional patterns among environment samples, in particular when many chemical parameters are available for the samples (Yunker et al., 1995; Xue et al., 2011). Here we applied PCA on the 5 sediment samples with the data matrix compiled with the concentrations of individual PAHs. Principle component 1 (PC 1) explains 57% of the data variances, and PC2 22% of the rest variance (Fig. 5). Clearly, the Aransas Bay sediment is well separated from the rest of the samples along the x-axis. Specifically, PAHs with high-numbered rings such as benzo[*b*]fluoranthene, fluoranthene, pyrene, and benzo[*a*]anthracene were relatively enriched in the Aransas Pass sediments, consistent with the results shown in Fig. 4. Mesquite Bay sediments were separated from the rest of sediments along the PC2 because of its enrichment in 2-methyl-naphthalene and fluorene, the two low-molecular-weight PAHs.

3.3. Sources of PAHs

The composition of PAHs can be used to derive the contamination sources, such as those from pyrolytic origins due to combustion processes *vs.* petrogenic sources such as oil spills. The dominance by naphthalene (2 rings) and phenanthrene (3 rings) (Fig. 3) suggests that these sediments were contaminated by petroleum sources through either non-point sources of oil spills such leakage from boats or atmospheric deposition (Blumer and Youngblood, 1975). However, the Aransas Bay sediment must have another major source because of its enrichment in PAHs with high number of rings (Figs. 4&5). This additional source can be attributed to pyrolytic origins, such as incomplete combustion of fossil fuels, which is also supported by the facts that a ratio of Phe/Ant <10 (Table 1) (Benlahcen et al., 1997). While the exact pyrolytic source to PAHs in the Aransas Bay sediment is unclear, we suspect that it may be impacted by incomplete combustion of fossil fuels caused by more shipping activities in the Aransas Bay than other

sampling locations. For example, all ship traffic, with a major fraction as oil tankers, enters the Port of Corpus Christi, the sixth largest port in the United States, through the Port Aransas Ship Channel, located physically much closer to the Aransas Bay. The contaminated water from Corpus Christi Bay and the ship channel would exchange with waters in the Aransas Bay more easily than with waters from other locations due to the physical distance. More spatial coverage is needed to further test this hypothesis.

4. Conclusions and Future Work

Our study showed that the total concentrations of 16 US EPA PAHs plus the two alkylated ones ranged from 103.7-195.4 ng g⁻¹ in surface sediments of 5 sampling stations within the Mission Aransas NERR. This concentration range is at the low end of contamination ranges typically found in estuaries and coasts, and would not be expected to cause biological degradation. While the compositions of PAHs in these sediments suggest combustion or petroleum source contamination, the PAHs in the Aransas Bay sediment were relatively enriched with the ones with high number of rings. This indicates an additional pyrolytic origin of PAHs to the Aransas Bay sediment. One possibility is the incomplete combustion of fossil fuel caused by the shipping activities within this area. More spatial coverage of the sampling stations would help to test this hypothesis.

Further chemical analyses for alkylated PAH homologous series can help determine the contamination sources of oil vs. soot (Wang et al., 1999). Ancillary chemical parameters such as organic carbon contents and grain size distribution can also help to decipher the geochemical behaviors of PAHs. This study only addressed the surface sediment, within 10 years of time

span, so depth profiles would be helpful to decipher the historical temporal changes of PAHs within the Mission-Aransas NERR.

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Table 1. Concentrations of 18 USEPA priority PAHs in the 5 samplings stations within the Mission-Aransas NERR (unit: ng/g dried weight sediment). Reported here are the averaged values of duplicate analyses of sediment samples. Phe/Ant and Fl/Py are the concentration ratios of Phenanthrene (Phe) over Anthracene (Ant), and Fluoranthene (Fl) over Pyrene (Py).

PAHs (ng g ⁻¹)	Aransas Bay	Copano West	Copano East	Mesquite Bay	Mesquite Channel
Naphthalene	21.0	15.5	20.4	20.7	18.5
Naphthalene, 1-methyl-	7.3	4.3	7.9	4.5	8.9
Naphthalene, 2-methyl-	7.4	3.9	1.8	8.4	3.1
Acenaphthylene	16.9	11.8	11.6	5.8	7.9
Acenaphthene (Ace)	3.6	3.1	5.7	3.3	4.5
Fluorene	5.3	3.8	3.0	6.6	2.8
Phenanthrene (Phe)	32.9	21.5	25.7	28.1	21.6
Anthracene (Ant)	3.8	1.8	1.6	0.6	1.8
Fluoranthene (Fl)	19.1	10.9	11.1	11.5	7.6
Pyrene (Py)	17.8	8.2	8.8	10.7	8.0
Benz[a]anthracene	8.8	1.5	2.8	5.3	2.9
Chrysene	8.5	3.6	5.9	5.6	2.6
Benzo[b]fluoranthene	17.8	6.0	6.6	7.3	5.2
Benzo[k]fluoranthene	4.0	4.1	2.7	1.6	0.9
Benzo[a]pyrene	8.7	2.7	2.9	7.0	2.8
Indeno[1,2,3-cd]pyrene	7.1	4.0	4.8	0.4	1.0
Dibenz[a,h]anthracene	3.2	1.2	1.4	2.1	2.3
Benzo[ghi]perylene	2.1	0.9	2.3	0.8	0.5
Total concentration	195.4	108.9	127.0	130.3	102.7
Phe/Ant	8.7	11.9	15.7	46.7	12.2
Fl/Py	1.1	1.3	1.3	1.1	0.9

Figure Captions

Figure 1. The map of Mission-Aransas National Estuarine Research Reserve (NERR) (Modified from 2006 program report of NOAA). The red circles are the sampling stations including Aransas Bay, Copano West, Copano East, Mesquite Channel, and Mesaquite Bay.

Figure 2. Total concentrations of PAHs in the 5 stations within the Mission-Aransas NERR. Error bars represent 1 standard deviation of duplicate analyses of sediments.

Figure 3. Composition of the 18 PAHs in the surface sediments collected at the 5 stations within the Mission Aransas NERR.

Figure 4. Concentration of PAHs in the surface sediments of the 5 sampling stations within the Mission Aransas NERR. The PAHs were grouped according to the number of rings within their structures: (a) with 2 rings including naphthalene, 1/2 methyl-naphthalene; (b) with 3-4 rings including acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene; (c) with 5-6 rings including benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene.

Figure 5. Principal component analysis (PCA) on the 18 PAHs in surface sediments from the 5 sampling stations within the Mission-Aransas NERR. The data matrix for the PCA was compiled by the concentrations of individual PAHs. PC 1 explains 57% of the data variances, and PC2 22% of the rest variance. It can be clearly seen that Aransas Bay sediment had different PAH compositional pattern than the rest sediments.

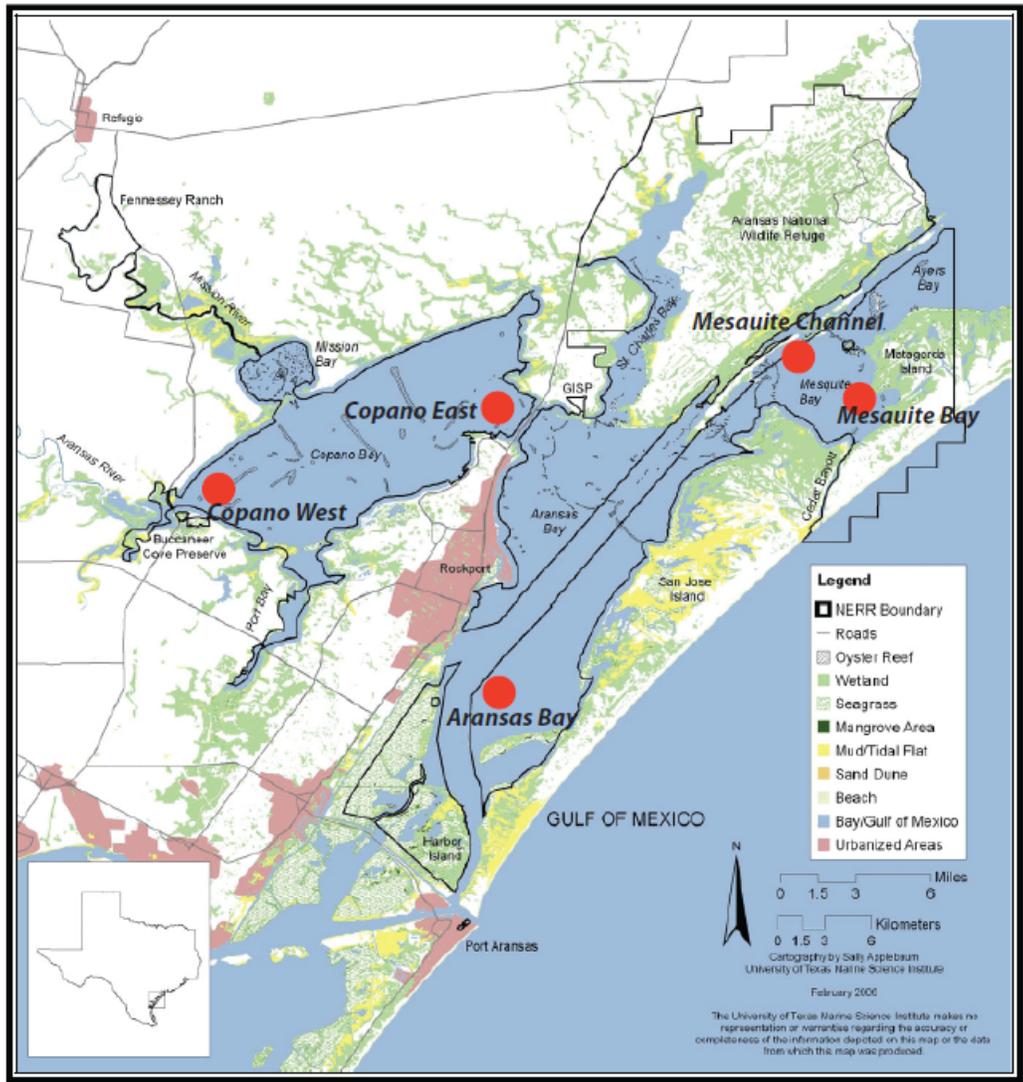


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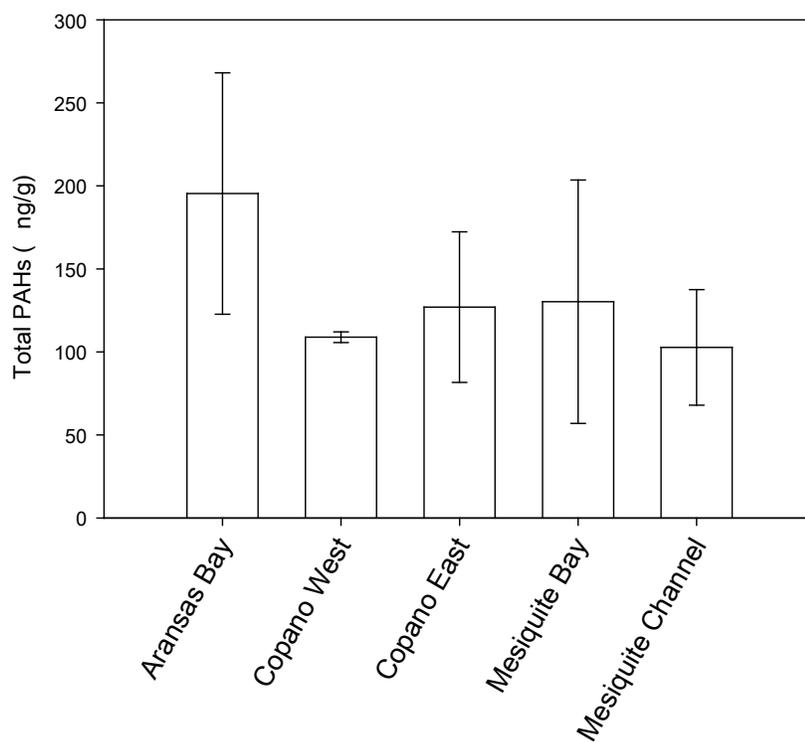


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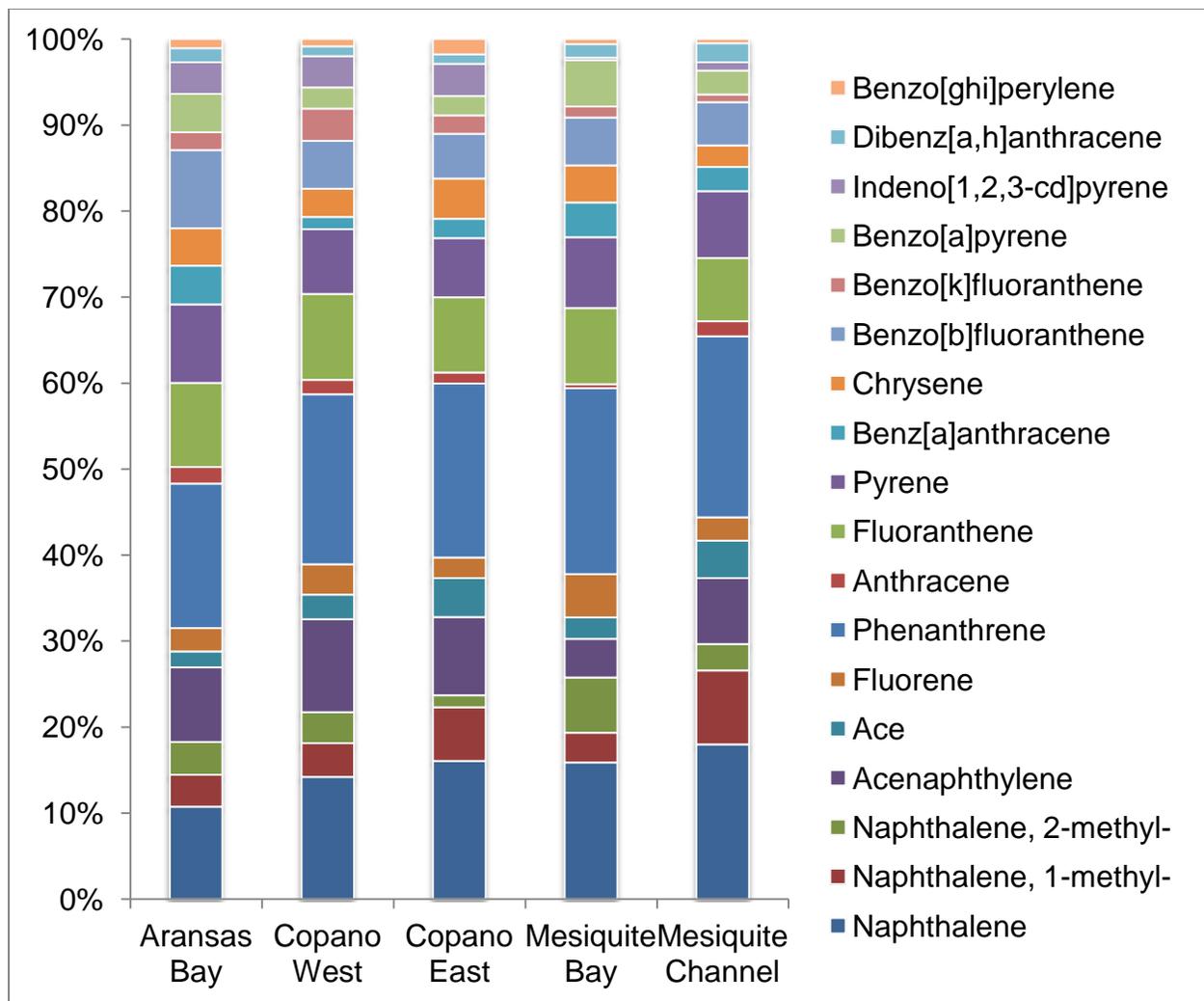


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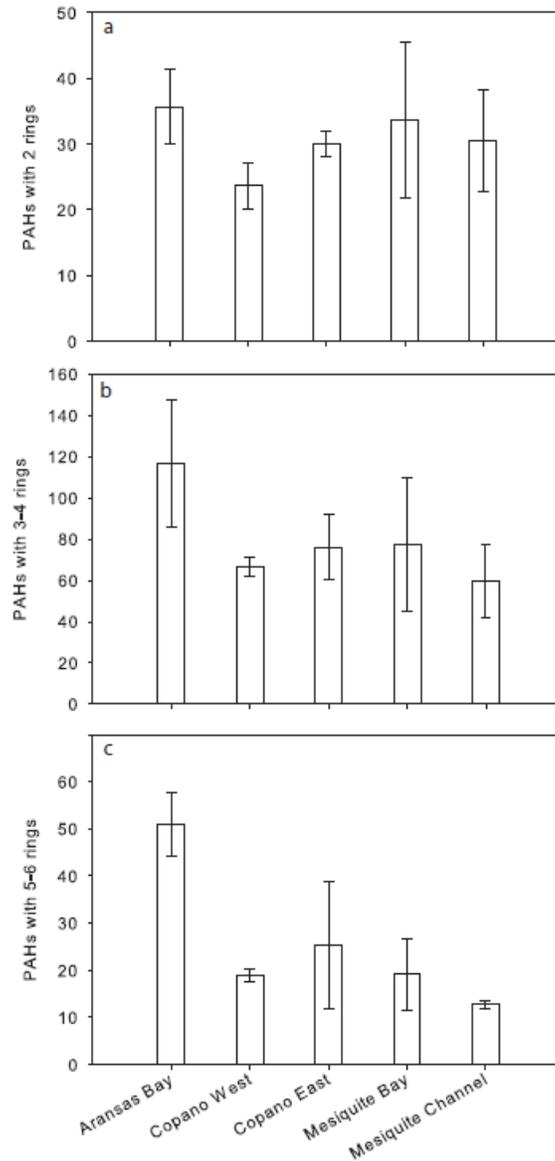


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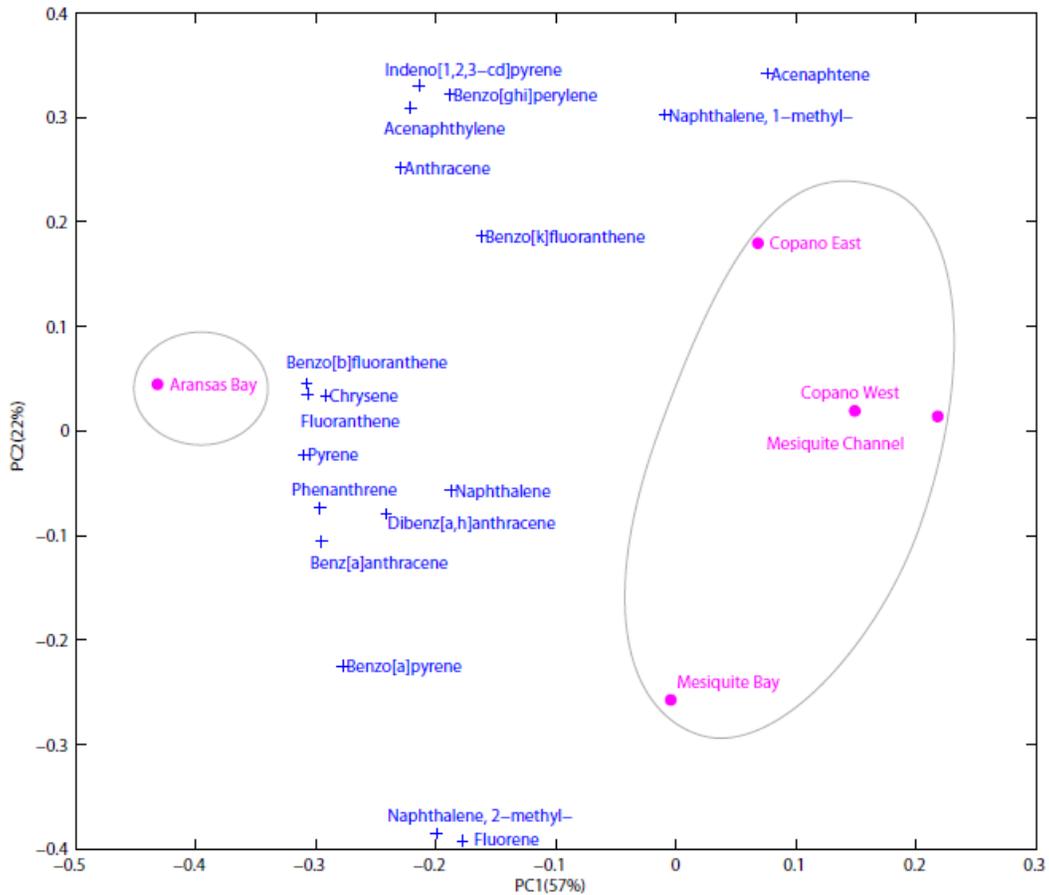


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