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Authors

Neira, Carlos
Cossaboon, Jennifer
Mendoza, Guillermo
et al.

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**Occurrence and distribution of polycyclic aromatic hydrocarbons in surface
sediments of San Diego Bay marinas**

Carlos Neira^{1*}, Jennifer Cossaboon², Guillermo Mendoza¹, Eunha Hoh², Lisa A. Levin¹

*¹Integrative Oceanography Division and Center for Marine Biodiversity and
Conservation, Scripps Institution of Oceanography, La Jolla, California, USA*

*²Graduate School of Public Health, San Diego State University, San Diego, California,
USA*

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) have garnered much attention due to their bioaccumulation, carcinogenic properties, and persistence in the environment.

Investigation of the spatial distribution, composition, and sources of PAHs in sediments of three recreational marinas in San Diego Bay, California revealed significant differences among marinas, with concentrations in one site exceeding 16,000 ng g⁻¹.

‘Hotspots’ of PAH concentration suggest an association with stormwater outfalls draining into the basins. High-molecular weight PAHs (4-6 rings) were dominant (>86%); the average percentage of potentially carcinogenic PAHs was high in all sites (61.4 - 70%) but ecotoxicological risks varied among marinas. Highly toxic benzo(a)pyrene (BaP) was the main contributor (>90%) to the total toxic equivalent quantity (TEQ) in marinas.

PAHs in San Diego Bay marina sediments appear to be derived largely from pyrogenic

sources, potentially from combustion products that reach the basins by aerial deposition and stormwater drainage from nearby streets and parking lots.

Keywords: Polycyclic aromatic hydrocarbons; surface sediment; spatial distribution; pollution; marina; San Diego Bay

* Corresponding author.

E-mail address: cneira@ucsd.edu (C. Neira)

1. Introduction

The growth of recreational boating in coastal areas has raised concern about potential contamination of waterways (USEPA 2001). Marina basins are exposed to contamination from a series of pollutants; including petroleum hydrocarbons. These enter aquatic environments through multiple activities such as refueling operations, repair of boat engines and boat maintenance, leaching of creosote-treated pilings, as well as input from stormwater runoff from parking lots and roads, and aerial deposition (Katz et al. 1995; Durand et al. 2004; Yilmaz et al. 2014). These not only degrade aquatic habitat, water quality and aesthetics but also generate additional costs to federal, state and local agencies for containment and cleanup (GESAMP 1990).

The primary petroleum product constituents most toxic to aquatic organisms are polycyclic aromatic hydrocarbons (PAHs), which due to their lipophilic character (low solubility), tend to be adsorbed onto particles in marine water and ultimately accumulate in sediments (Antizar-Ladislao 2009; Sugahara et al. 2014). Although naturally occurring, PAHs are mainly generated from anthropogenic sources. They enter the environment during the incomplete combustion of fossil fuels, organic materials, e.g. wood, grass, coal (pyrogenic) containing a wide range of molecular weights, through the release of crude and refined petroleum (petrogenic) dominated by low molecular weight compounds (e.g. Baumard et al. 1999; Soclo et al. 2002; Pampanin and Sydnes 2013). They also are derived from early-diagenetic transformation of biogenic precursors such as natural products produced by higher plants. For instance, retene is derived from the diterpenoid abietic acid, biogenic phenanthrene is derived from the diagenesis of steroids and

dealkylation of retene, alkylated hydrochrysenes are derived from triterpenes, and perylene is suggested to be produced by a mix of terrestrial and aquatic precursors, with fungi as the biological source agents (Tan et al. 1996; Zhang et al. 2014; Wakeham and Canuel 2015).

Once the PAHs enter the marine environment, they can then readily be taken up by marine biota (Perugini et al. 2007; Martinez-Gomez et al. 2010; Liu et al. 2015) either through their gills or via ingestion (Baumard et al. 1999). The main mechanism underlying toxicity of PAHs is their direct binding to hydrophobic sites of macromolecules such as lipids, proteins, and nucleic acids, interfering with their normal functioning (Vijayavel et al. 2004; Pampanin and Sydnes 2013). Sixteen PAHs have been listed as pollutants of concern by the United States Environmental Protection Agency (US EPA) (Haritash and Kaushik 2009) because of their toxicity and their potential carcinogenic, mutagenic and teratogenic properties (White 1986; Quiao et al. 2006); they are of high priority for environmental pollution monitoring.

San Diego Bay (SDB), California, USA is an important commercial port harboring military shipping activities, a substantial commercial fleet, and intense recreational boating. Due to its urbanized surroundings and multiple uses, SDB is subjected to several contaminants of concern. It has been listed as an impaired water body under the US EPA Clean Water Act Section 303[d] due to elevated levels of pollutants in sediments and biota (Fairey et al. 1998), and ranked as one of the most contaminated urbanized coastal areas in the nation (O'Connor 1990). Primary areas of concern are outlets of creeks, shipyards, and marinas (U.S. Navy, NAVFAC, UPSD

2013). In SDB, organic pollutants such as PAHs tend to accumulate in sediments with the potential to alter faunal community structure and to impair beneficial uses for the Bay. Various studies across SDB have identified relatively high levels of PAHs in Bay sediments (e.g. McCain et al. 1992; Fairey 1996; Zeng and Vista 1997; Exponent 2003; USFWS 2006; SPAWAR Systems Center 2007). Due to their often semi-enclosed character and poor flushing, marinas acts as “tidal traps” (Largier 1995) and hence sediments are considered the most important reservoir of PAH contaminants (Culotta et al. 2006). At a regional scale, it is estimated that 40% of the total PAHs found in surficial sediments of Southern California Bight are present in the bays and harbors, representing 5% of area (Stein et al. 2006).

The actual levels of PAHs in marina basins and potential ecological consequences are of increasing interest. Marinas are not only subjected to typical boating operations (e.g. fueling, oil change, repair) that can cause leaking and small spills of hydrocarbons (Johnson 1998), but they also receive stormwater runoff from adjacent urban, often densely populated areas; these influences elevate PAH fluxes to aquatic environments (Crepineau-Ducoulombier and Rychen 2003; Van Metre et al. 2009; Sulej et al. 2011; Traven 2013; Yilmaz et al. 2014). Therefore, the identification of local sources is critical for evaluating the risk of contamination by PAHs and their impact on the environment and human health. Anthropogenic inputs of PAHs into SDB marinas have led to concerns about the ecological effects associated with sediment quality. Thus, in this study we addressed the following questions: (1) What is the actual concentration of PAHs in surface sediments of three SDB marinas? (2) Does the PAH composition differ among marinas? (3) How are PAHs spatially distributed? (4) Are there trends and hotspots of

PAH concentration associated with boat presence? (5) Do PAH levels in marinas represent a potential ecotoxicological risk? and (6) What are the possible sources of PAHs contamination?

2. Materials and Methods

2.1. Study sites

We determined the composition, concentration and spatial distribution of PAHs in surface sediments at three marinas located in the north section of SDB (32°40' N, 117°4'W) (Fig. 1). Shelter Island Yacht Basin (SIYB) is a semi-enclosed basin ~3.2 km long, 0.475 km wide, and ~5 m deep, with its opening facing the main entrance channel of SDB (CARWQCB 2005; Neira et al. 2009). Harbor Island is located south of SIYB and consists of two embayments: Harbor Island West (HW), about 1.46 km long, ~0.28 km wide, and ~4.2 m deep; and Harbor Island East (HE), about 0.73 km long, 0.167 km wide, and ~4.1 m deep; the mouth faces to the east (Neira et al. 2014). All three marinas have relatively well-flushed mouths but restricted water mixing at the heads (Zirino et al. 1998). Water residence times, along the main channel, are estimated to be 5-6 days for SIYB and 8-11 days for Harbor Island (Chadwick et al. 2004).

2.2. Sampling design

Field sampling was conducted in summer (July) 2014 in order to examine actual

PAH concentrations in the sediments of the three marinas. The late spring/summer period coincides with increasing boating activity and maintenance (Neira et al. 2009), the weakest flushing and circulation, and the longest expected residence times (Largier 1995). A total of 43 stations covering the three basin waterways were sampled, spanning open areas and moored motor craft areas. Twenty stations were located in SIYB, 15 in Harbor Island West, and 8 in Harbor Island East (Fig. 1). Coordinates and sediment properties of each station are shown in Table 1.

2.3. Sample collection and processing

Samples of surface sediment (0-5 cm depth) were collected at each station with a small custom-made gravity corer (surface area 20.4 cm²) deployed from a small boat. Onboard, a fraction of surface sediment (~60 cc) was transferred to a short, wide-mouth, amber-colored glass jar, certified to meet US EPA specifications (300 series) (Fisher Scientific), sealed, and transported in a cooler to the laboratory and stored in a freezer at -20°C until analysis. A second fraction from the same corer was transferred to a polypropylene tube and used for determining organic carbon, total nitrogen, phytopigments, water content, and grain size. Water content was determined by weight loss after freeze-drying a pre-weighed aliquot of wet sediment. Total organic carbon (TOC) and total nitrogen (TN) were determined from freeze-dried, homogenized sediment, using a Costech CHN analyzer (Valencia, CA) after removal of inorganic carbonates. Sediment chlorophyll *a* (chl *a*) and phaeopigments were determined fluorometrically from freeze-dried sediment (Hagerthey et al. 2006) after extraction with

90% acetone (Danovaro 2010). Percent silt-clay (< 63 μm) and sand (> 63 μm) were determined by wet sieving sediment aliquots as described by Neira et al. (2009).

2.4. Chemicals, reagents and standards

All solvents and reagents, trace analysis or ACS grade, were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Bond Elut QuEChERS AOAC Kits were purchased from Agilent Technologies, Inc. (Wilmington, DE, USA). Chemical mixture solutions for analytes and internal/recovery standards were purchased from AccuStandard (New Haven, CT, USA); perdeuterated PAH Internal Standard Mix (Z-014J-0.5X-PAK; naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂), and recovery standard mix (CLP-LC-SS1); nitrobenzene-d₅, 1,1'-biphenyl-2-fluorene-d₁₀, and *p*-terphenyl-d₁₄). The analytes, abbreviations, and corresponding product numbers are listed in Supplementary material Table S1.

2.5. Sample extraction

Sediment samples were thawed, homogenized, and prepared using a modified QuEChERS method (Quick Easy Cheap Effective Rugged and Safe; Anastassiades et al. 2003; Payá et al. 2007) AOAC approach for extraction and cleanup of pesticide residues. Sample aliquots of ~5 g (wet weight) were transferred to 50 mL cleaned-glass centrifuge vials. Samples and procedural blanks were spiked with 200 μL of PAH internal standard mixture for compound quantification at 1 ng/ μL and vortexed for 5 min with 3 mL of

LC-MS Grade Water. After letting the samples rest for 30 min, they were vortexed for 5 min with 5 mL of ethyl acetate. Next, 3.75 g of Agilent Bond Elut QuEChERS extraction salts (PN 5982-5755) containing anhydrous MgSO_4 and anhydrous NaOAc at 4:1 were added to each sample and vortexed for 5 min. Samples and blanks were then centrifuged at 2000 RPM for 15 min. The resulting organic aliquot extract layer was transferred to cleaned glass test tubes and concentrated to ~1 mL using nitrogen on a Turbo Vap LV evaporator (Biotage AB, Charlotte, NC, USA) set at 60°C. Extracts were transferred to QuEChERS dispersive solid phase extraction (dSPE) 2 mL tubes (PN 5982-5058) containing 50 mg of PSA and 150 mg of anhydrous MgSO_4 for further cleanup and shaken vigorously by hand for 1 min. After centrifugation (10,000 rpm $\times$ 1 min), the liquid aliquot extract layer was concentrated down to 400 μL , and then was spiked prior to instrumental analysis with 50 μL of a recovery standard mix at 1 ng/ μL .

2.6. Instrumentation for PAH analysis

A GC x GC/ToF-MS Pegasus 4D (LECO, St. Joseph, MI, USA) equipped with an Agilent 6890 GC with a secondary oven, a splitless injector, and a non-moving quad-jet dual stage modulator was used for PAH characterization. Detailed information regarding the instrumental parameters is listed in Supplementary material Table S2. The instrumental parameters were previously optimized (Manzano et al. 2012) and multiple point calibration curves were used, using the same approach as described by Manzano et al. (2013).

A total of 36 PAHs were quantified in this study, including 15 of the 16 of the PAHs categorized as priority pollutants by the World Health Organization, the European Economic Community, and the US Environmental Protection Agency (Hellow 1996). Parent PAHs (i.e. unsubstituted two or more fused conjugated rings) and other 22 non-parent PAHs (i.e. PAH with various alkyl groups attached) are listed on Supplementary material Table S1. Benzo(b)fluoranthene and benzo(k)fluoranthene were combined and listed as benzo(b+k)fluoranthene. Dibenz(a,h)anthracene did not elute within the instrumental run time; thus only 14 parent PAH analytes are listed.

The limit of quantification (LOQ) of the PAHs in the samples ranged from 0.017 to 40 ng g⁻¹. The LOQ varied for individual PAHs and is listed for each compound on Supplementary material Table S3. The individual concentrations of PAHs in sediment are in ng g⁻¹ on a dry weight basis.

2.7. Quality assurance and quality control

All glassware was cleaned and baked at 450°C for 6 h. A strict quality control procedure was conducted during PAH analysis consisting of a procedural blank for each set of prepared samples and an internal calibration method for quantification of parent and non parent PAHs using surrogate standards. Calibration standard solutions were analyzed at the beginning, middle and end of each instrumental set of samples, and five-point calibration curves with a range of 5 – 1280 pg/μL were constructed as formerly described (Manzano et al. 2013). The reported concentrations are blank and recovery corrected. The method recoveries for the five internal PAH standards averaged 60 ±30%.

2.8. Data analysis

Correlations among investigated PAHs and environmental variables were evaluated with the Spearman's rank correlation coefficient (Zar 1996). One-way analysis of variance (ANOVA) was used to test for differences in concentrations of PAHs within marinas. Data were transformed to achieve normality homogeneity of variances when necessary. The non-parametric Wilcoxon test was used when transformed data failed to fulfill parametric assumptions. Spearman and ANOVA analysis were conducted with the JMP Pro 12.0.1 software package. In addition, by using permutational ANOVA (perANOVA; Anderson 2008), a series of pairwise tests were performed to test for differences of PAHs (LPAH, HPAH, PPAH, TPAH and C-PAH) among marinas. In order to overcome normality issues and different sample size per marina, a Monte Carlo permutation test was performed. Univariate data were square root transformed. Analysis was conducted with the PERMANOVA add-on (Anderson et al. 2008) to a Primer v6 software package (Clarke and Gorley 2006). Spatial patterns of PAH similarity composition in relation to sites were examined using Principal Component Analysis (PCA).

Molecular indices involving concentration ratios of frequently found key PAHs were used to identify potential sources of PAHs (e.g. Burzinski et al. 1997; Soclo et al. 2000; Zemo 2009; Liu et al. 2015). The “forensic” source attribution used in this study was based on priority PAHs defined by the US EPA involving the combination of four molecular ratios involving anthracene (ANT), phenanthrene (PHE), fluoroanthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), indeno[1,2,3-cd]pyrene (IcdP),

and benzo[g,h,i]perylene (BghiP), and used to generate bivariate plots (e.g. Zemo 2009; Traven 2013, Rochman et al. 2013) to identify the sources of PAH contamination. The common ratios, $ANT/(ANT+PHE) < 0.1$, $FLA/(FLA+PY) < 0.4$, $BaA/(BaA+CHR) < 0.2$, $IcdP/(IcdP+BghiP) < 0.2$ indicate predominantly petrogenic source; while ratios $ANT/(ANT+PHE) > 0.1$, $FLA/(FLA+PY) > 0.5$, $BaA/(BaA+CHR) > 0.35$, and $IcdP/(IcdP+BghiP) > 0.5$ suggest combustion sources of biomass (e.g. coal, wood, grass). Values in between are suggested to originate from a combination of incomplete combustion of petroleum (e.g. engines) and modern biomass sources (e.g. wood, grass, cooked food over flame), $FLA/(FLA+PY) 0.4-0.5$ and/or $IcdP/(IcdP+BghiP) 0.2-0.5$ (Yunker et al. 2002; Chen et al. 2012; Keshavarzifard et al. 2014; Liu et al. 2015). PAHs with 3, 4, and 5 rings usually dominate emissions from both wood-burning and vehicle exhaust, because larger molecules tend to be incorporated into soot particles (Richter and Howard 2000). In addition, burning conditions can significantly influence the amount of each PAH produced (Lima et al. 2005). Additionally, the ratio of low molecular weight PAHs ($LPAH = \sum NAP + ACE + ACY +, FLO + PHE + ANT$) to high molecular weight PAHs ($HPAH = \sum FLA + PYR + BaA + CHR + BaP + DahA + IcdP + BghiP$) was used as an index for source identification because PAHs derived from petroleum (of petrogenic origin) are dominated by LPAH (2 to 3 rings), while PAHs from pyrogenic sources have higher molecular weights (4 – 6 rings). Thus, $LPAH/HPAH$ ratios < 1 indicate dominance of HPAHs; ratios > 1 indicate dominance of LPAHs (Magi et al. 2002; Scheibye et al. 2014).

Furthermore, to determine whether PAH levels represent a biological risk, results were evaluated by comparing concentration data to previously established sediment

quality guidelines (Long and Morgan 1990; Long et al. 1995). These guidelines identify Effects Range-Low (ERL) and Effects Range-Median (ERM). These guidelines are based on correlations between chemical concentrations and biological effects observed through an extensive review of toxicity tests involving benthic organisms, mostly *Ampelisca* (Long et al. 1995). Concentrations below the ERL value represent a minimal-effect range in which effects would be rarely observed. Concentrations equal to or above the ERL, but below the ERM, represent the possible effects-range in which adverse health effects would occasionally occur. Concentrations equal or above the ERM value represent a probable-effects range in which effects would frequently occur (Long et al. 1995). In addition, we explored the use of the equilibrium partitioning (EqP) sediment benchmark (= ESB) approach combined with the narcosis theory to estimate potential toxicity of mixtures of PAHs to the benthic fauna. Sediment toxic units (TUs) due to PAH were calculated according to US EPA 2003, 2012. Basically, the TUs of individual PAHs are summed together as narcotic chemicals such as PAHs are additive (Schultz et al. 1989). If the total number of TUs is > 1 , toxicity to benthic invertebrates is expected to occur (US EPA 2003). This approach was used to classify the sediments as Class A, when the total number of TUs is less than 1.0, i.e. sediment contaminant can be considered to present little or no potential risk to aquatic animal. If the total TU exceeds 1.0, then sediments are considered to be Class B, i.e. may represent a risk and further information is required or C, indicative of high potential for the sediments to be toxic to aquatic biota (DFWMR 2014).

In order to explore the potential toxicological risk levels of sediment PAHs, the toxic equivalent quantity of benzo(a)pyrene (BaP-TEQ) was calculated based on the

benzo(a)pyrene (BaP) toxic equivalents factors (TEFs) proposed by Nisbet and LaGoy (1992), where the TEF for each PAH is an estimate of the relative toxicity of the PAH compound compared to BaP. The TEFs were assigned to individual parent PAHs by assuming a relative value of 1 for BaP.

To produce probability maps of PAH spatial distribution, total PAH concentrations ($\Sigma 36$ PAH targeted) were interpolated on a regular grid by ordinary point kriging, which uses a weighted average of the neighboring points to estimate the value of an unobserved value (Sanders 2007). Kriging calculations were performed in Matlab 2008 (Trauth 2007) and then mapped using ArcGIS (ESRI, 2006). For the probability map of Harbor Island East, PAH data was Box-Cox Power transformed in order to normalize the data and make the color gradient smoother, ultimately facilitating the visualization of lower PAH concentrations.

3. RESULTS and DISCUSSION

3.1 PAH concentration in sediments

The concentration of the PAHs quantified in surface sediments of three marinas are presented in Table 2 and Supplementary material Tables S4, S5, and S6 for Shelter Island Yacht Basin (SIYB), Harbor Island West (HW), and Harbor Island East (HE), respectively. On average total PAH concentrations (sum parent + non parent) amounted to 1,086 ng g⁻¹ for SIYB (range 371 – 3,001 ng g⁻¹), 818 ng g⁻¹ for HW (range 411 – 1,412.4 ng g⁻¹), and 3,798 (range 622 – 16,663 ng g⁻¹) for HE (Fig. 2). Concentrations in

HE were significantly higher than in HW ($t = 3.07$, $P = 0.002$) and SIYB ($t = 2.40$, $P = 0.014$); no significant differences in total PAH concentration occurred between HW and SIYB ($t = 1.05$, $P = 0.293$) (PerANOVA tests).

PAH concentrations measured in the present study are comparable with early studies conducted in selected sites located inside marinas or adjacent to marinas along SDB main channel, which ranged 311 to 5000 ng g⁻¹ in sediments (e.g. McCain et al. (1992; Fairey et al. 1996; Zeng and Vista 1997; Kennish 1997; Katz 2007). In mid SDB, PAH concentrations in sediments from the Naval Station region, NASSCO and Southwest marine shipyards, and some sites at Chollas Creek and Paleta Creek were reported to be 508 to 94,200 ng g⁻¹ (Katz et al. 1995; Fairey et al. 1996; Chadwick et al. 1999; Chadwick and Largier 1999; Exponent 2003; Greenstein et al. 2011).

Overall total PAH concentration was positively correlated with sediment TOC content across all marinas ($r = 0.630$; $P < 0.001$). However, considering each marina individually, the correlations were significant in SIYB ($r = 0.792$; $P < 0.001$) and HW ($r = 0.604$; $P = 0.022$), but not significant in HE ($r = 0.678$; $P = 0.093$) (highest value of station HE08 not included in the analysis for visualization of the general pattern) (Fig. 3). When HE08 is included the correlation turns very weak ($r = 0.119$; $P = 0.778$). The small sample size of HE may influence the robustness of the correlation. The processes that govern PAH concentration in sediments are complex and factors such as TOC content affect PAH distribution (Yang et al. 2000). The positive correlation of total PAH concentration with TOC suggests that TOC may play an important role in controlling PAH concentrations and bioavailability (Luo et al. 2006) in SIYB and HW sediments. This positive correlation has been observed in sediments of other regions such as the

Yangtze River estuary (Wang et al. 2015), Pearl River estuary and adjacent coastal areas (Luo et al. 2006), as well as marinas and shipyards along the coast of Turkey (Okay et al. 2014). However, there are several studies on coastal sediments that do not follow this pattern (e.g. Tam et al. 2001; Raza et al. 2013). These different PAHs-TOC relationships may be influenced by the contribution of different PAH compounds according to the number of aromatic rings. For instance, concentrations of low molecular weight PAHs (2-3 rings) decrease with increasing organic carbon, medium molecular weight PAHs (i.e. 4 rings) are not or are only marginally influenced by organic carbon, while PAHs with 5 or more rings increase with increasing organic carbon concentration (Moeckel et al. 2014).

Mud content ($< 63 \mu\text{m}$) is considered another important factor controlling PAH concentrations (Burton et al. 2012), as multi-ringed PAHs tend to absorb better to fine-grained fractions (Akerblom et al. 2010). As for TOC, a modest but significantly positive correlation was observed between mud and total PAHs in SIYB ($r = 0.583$; $P = 0.006$), HW ($r = 0.644$; $P = 0.012$), however not in HE ($r = 0.404$; $P = 0.319$). In spite of the small sample size in HE, the poor correlation observed is in line with the narrower range in sediment grain size (29.6-75.8%) and TOC (0.52-1.65%) relative to SIYB and HW. The highest PAHs concentration observed at station HE08 occurs in sediments with relatively low TOC and mud content (Table 1). This suggests a local source, most likely small storm drains adjacent to the PAH concentration hotspot near the mouth of the marina (Fig. 6C). The high concentration of PAHs at station HE08, where TOC is relatively low may be explained by outfalls introducing direct dry or wet deposition and runoff-mediated input of LPAH (2 to 3 rings) and more volatile 4-ring PAHs with low

affinity for organic carbon such as fluoranthene and pyrene (Fig. 5C). The types of organic matter may also affect PAH concentrations in sediment. Organic matter in sediments such as humic substances, geopolymers and combustion-derived products have different sorption and desorption capabilities (Rockne et al. 2002; Cornelissen et al. 2005; Yang et al. 2011; Wang et al. 2014). Different flocculation rates of particles, as well as the proximity to the contaminant source, have been suggested to contribute to the differences in sedimentary PAH loads (Kucklick et al. 1997; Wang et al. 2015).

Parent PAHs accounted for over 96% of the total 36 PAHs targeted in this study; conversely, non-parent (alkylated) PAHs represented less than 4% of the total. Reports indicate that in crude oil as much as 98% of the total PAHs are alkylated, and in petrogenically-contaminated sediments these can amount to 70% (Budzinski et al. 1997; Hawthorne et al. 2006). Three of 5 individual non-parent PAHs with quantifiable concentrations (2,6-dimethylnaphthalene, 2-methylanthracene and 6-methylchrysene) were present and common for HW and HE (Supplementary material Tables S5 and S6, respectively). SIYB showed, in addition, 1-methylphenanthrene and 1-methylpyrene, although in some stations only (Supplementary material Table S4). Average concentrations of non-parent PAHs for HE (62 ng g^{-1}) were significantly higher than for HW (33 ng g^{-1}) and SIYB (28 ng g^{-1}) ($F_{2,41} = 6.5$, $P = 0.003$). All stations of the three marinas show occurrence of 2,6-dimethylnaphthalene, an alkyl homolog of naphthalene. Alkylated naphthalenes are found in crude and fuel oils, and coal tar. Naphthalene and alkylated naphthalenes are especially hazardous in the aquatic environment due to a combination of features such as mobility and toxicity (e.g. Sarojini et al. 1995; Vijayavel et al. 2004). They have been implicated in the toxicity to polychaetes (Rossi and Neff

1978; Rust et al. 2004), bivalves (Bender et al. 1988; Granby and Spliid 1995), shrimps (Dillon 1981; Jaward et al. 2012) and fish (Schnell et al. 1980; Incardona et al. 2004).

The concentrations of high molecular weight PAHs (HPAHs; 4-6 rings) were significantly higher than the concentrations of low molecular weight PAHs (LPAHs; 2-3 rings) in all three marinas. On average, HPAH and LPAH concentrations were 947 and 112 ng g⁻¹ for SIYB ($X^2 = 29.2$, $df = 1$, $P < 0.0001$), 716.72 and 68.07 ng g⁻¹ for HW ($X^2 = 15.8$, $df = 1$, $P < 0.0001$), and 3066 and 670 ng g⁻¹ for HE ($X^2 = 7.4$, $df = 1$, $P = 0.006$), respectively. Previous studies in SDB have shown a similar trend, with higher concentrations of HPAH relative to LPAH (McCain et al. 1992; Fairey et al. 1996).

On average, carcinogenic PAH (C-PAH: BaA, CHR, BbKF, BaP, IcdP) concentrations in surface sediments were 737 ng g⁻¹ for SIYB, 554 ng g⁻¹ for HW and 1221 ng g⁻¹ for HE. PerAnova tests revealed that concentration of C-PAH in HE was significantly higher than in HW ($t = 2.64$, $P = 0.010$), while no significant differences in C-PAH concentrations were observed between HW and SIYB ($t = 1.01$, $P = 0.322$) or HE and SIYB ($t = 1.59$, $P = 0.111$). The contribution of US EPA potential carcinogenic PAHs (Σ chrysene, benzo(a)anthracene, benzo(b,k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene) to the total parent PAHs was relatively high, an average of 69.2%, 70%, and 61.4% for SIYB, HW, and HE, respectively (Supplementary material Tables S4, S5, and S6).

3.2. PAH composition and spatial distribution

The distribution pattern by number of aromatic rings (parent and non-parent),

separated in four groups, namely 2 and 3- ring, 4-ring, 5-ring and 6-ring PAHs, for each marina showed a relative uniformity as shown in Fig. 3A, 3B, and 3C. Overall 4- to 6-ring PAHs predominated in marina sediments, comprising about 86%. Within these high molecular weight congeners, 4-ring PAHs were the main contributors with 46.8% in SIYB and 49.9% in HE; while in HW 5-ring PAHs were the most abundant with ~42% of the total PAHs. The abundance of high molecular-weight 6-ring PAHs was on average ~10% for the three marinas. Only a few stations had relatively unique distribution patterns as indicated by PCA analysis (not shown). In SIYB station SI12 the relative abundance of 4-ring PAHs was relatively low ~18% while 5- and 6 ring-PAHs were higher than other stations, at 47% and 27%, respectively (Fig. 4A). Conversely, a shift in ring size distribution observed in SIYB station SI01 involved an increased abundance of 4-ring PAHs (up to 63.6%), but reduced contribution of 2- and 3-ring (3.9%) and 6-ring PAHs (7.5%) to the total PAHs. Station HE08, located adjacent to the mouth exhibited a distinctly different composition, with predominance of 3- and 4-ring (72.5%) followed by 2- and 3-ring (25.5%) PAHs, in addition to having the highest levels of PAH in sediments measured in this study (Fig. 4C).

Contribution of individual PAH constituents also revealed a relative uniformity in PAH composition, with the same few stations as for ring size (i.e. SI01, SI12, HW01, HE08) depicting a different pattern (**Fig. 4A-C**). This suggests a similar source or suite of sources for the PAHs in most of the marina sites.

The spatial distribution of total PAH for each marina is shown in Fig. 6A, 6B, and 6C. There are different concentration ranges for each marina, and the “hotspot” gradients do not follow the distribution of moored boats (Fig. 1), as is the case for copper in

sediment (Neira et al. 2009; 2014). In HW, the highest concentrations were detected at stations HW05, HW03, and station HW01, located near a busy road and adjacent parking lots (Fig.1). Station HW08 (adjacent to a parking lot near the mouth). Interestingly, station HW10 located near to a fueling station at the mouth had the lowest total PAH concentrations (411 ng g^{-1}), while the area of station HW08 located toward the interior and adjacent to a parking lot, showed a PAH hotspot (Fig. 6B). Low PAH concentration at the station HW10 was consistent with lower mud and TOC content relative to station HW08 (Table 1).

In general, the occurrence, composition and spatial distribution of PAHs in the marine sediment environment reflect the extent and magnitude of organic contamination by PAHs. Once PAHs enter the marine environment, their fate depends on multiple factors such as the volatility of the compound and hydrodynamics of the receiving water. The similar assemblages of PAHs, with a higher abundance of non-alkylated PAHs, dominated largely by high molecular-weight PAHs, suggest inputs from incomplete combustion of fuels (e.g. diesel, gasoline) and biomass (e.g. coal, wood, grass), motor oil and exhaust systems (Schauer et al. 2002). The PAHs in sediments are good indicators of anthropogenic activities occurring at marina basins and in surrounding urban areas. Multiple factors can influence the spatial distribution of PAHs, including quantity and quality of organic matter, sediment grain size, and PAH sources (Cornelissen et al. 2005). The general relationship of sediment TOC content with PAH concentrations suggests that TOC could influence the spatial distribution of PAH concentrations; however, it is likely that all of these factors collectively play a role in determining the fate, transport and spatial distribution of PAHs in marina sediments.

3.3. Ecological and toxicological risk assessment

In this study, the concentrations of individual PAHs in SIYB and HW were largely below the ERL. In contrast, HE had concentrations of several PAHs between ERL and ERM, and above the ERM for PHE, ANT, PYR and BaA (Table 3). In HE, total PAHs, LPAH and HPAH exceeded the ERL at station HE01, and exceeded the ERM at station HE08 (Table 3). These suggest that at some selected sites at HE, adverse ecological effects would occur occasionally, and that a potential ecological risk is posed by some individual PAHs. While the two effects-based guidelines are widely used to assess ecological risk posed by PAHs in marine sediments, comparisons with guidelines should be taken with caution since sediment quality guidelines are based on empirical relationships, and any exceedance will not necessarily reflect causality. Further use of the US EPA equilibrium partitioning sediment benchmark approach (US EPA 2003) revealed that the sum of toxic units in all stations of SIYB were below the value of 1.0 (Supplementary material Table S4) and thus sediment would be considered of low risk for benthic animals (Class A). In contrast, in HW, 7 stations presented values above 1.0 (Supplementary material Table S5) suggesting sediments to be potentially toxic (Class B). In HE, only the station HE08 adjacent to the mouth showed a toxic unit of 4.74 (Supplementary material Table S6), indicating that exposure to sediment PAHs exceeded chronic toxicity for benthic invertebrates (Class B). PAHs may be of concern due to possible toxicity for benthic biota exposed to sediment. Further studies are necessary to confirm whether these benchmarks are reflected on benthic community impairment. Elevated sediment benchmarks toxic units in several sites of HW and HE create concern

for potential effects on benthic communities. HE is located along a busy city parking lot harboring car rentals. Different composition, with predominance of 3-4 ring PAHs, as supported by the highest LPAH/HPAH ratio at station HE08 near the mouth where no boats are moored, suggests a nearby source such as stormwater runoff from car parking / maintenance lots draining into the basin. Similar situation occur for HW with parking lots from the nearby airport and other facilities. Parking lots are considered major contributor of PAHs in urban areas (Steuer et al. 1997; Lau and Stenstrom 2005). The specific responses to the PAHs will depend on the metabolic systems and sensitivities/tolerances to environmental stress of the individual species (Driscoll and McElroy 1996; Rust et al. 2004), and further studies will be required to elucidate specific sources and potential effects on sediment dwelling fauna.

The presence of PAHs in the environment may have ecological and health consequences not only for aquatic organisms but also for humans, as PAHs can enter the food chain. Persistent binding to macromolecules such as lipids in organism tissues make PAHs available for trophic transfer to higher trophic levels. In comparison to vertebrates (e.g. fish), invertebrates have a limited ability to metabolize PAHs (Rust et al. 2004). Table 4 shows BaP-TEQ (benzo(a)pyrene toxic equivalent) values calculated for all three marinas. Mean total BaP-TEQ values were 205 ng g⁻¹, 193 ng g⁻¹ and 363 ng g⁻¹ for SIYB, HW and HE, respectively. Among different PAHs, the most toxic, carcinogenic BaP was the main contributor to the total BaP-TEQ. Benzo(a)pyrene has been used as the reference chemical because its toxicity is well characterized and because it is considered one of the most potent carcinogens in the PAH class (Yang et al. 2014a). The contribution of BaP to the total was over 90%, followed by BaA and IcdP (>3%). The

percent contribution of potential carcinogenic PAHs deposited in SDB marina and harbor sediments (> 60% of total) deserves attention because PAHs, such as BaP, can be a potential risk for aquatic life. Total BaP-TEQ values in SDB are lower or comparable to the levels reported for other coastal areas of the world; these vary widely, from below detection to concentrations as high as 7049 ng g⁻¹ (e.g. Savinov et al. 2003; Yang et al. 2014b; Okay et al. 2014). PAHs are able to enter aquatic (and terrestrial) organisms through the skin, gills, lungs, and digestive tract and tend to accumulate in fatty tissues (Watanabe et al. 2005). The contribution of BaP is of concern due to acute and sublethal biological effects on sediment-dwelling fauna. Effects include DNA damage, endocrine disruption, sexual maturation inhibition, reproduction impairment due to decreasing fertilization, changes in sex ratio, and hatching reduction (e.g. Banni et al. 2010; Tian et al. 2013; Wen and Pan 2015; Wu et al. 2016). Thus, accumulation of PAHs in general, and BaP in particular, in marina sediments may cause disruption of biological processes with ecological and ecosystem consequences that merit further investigations. The use of multiple approaches to examine ecological risks in marinas revealed not only hotspot sites of PAH contamination and complexity of different marinas as with different toxicity thresholds but establishes priority sites that may merit further study.

3.4. PAH source diagnosis

The dominance of pyrogenic sources of PAHs in the marinas not only is supported by the overall low LPAH/HPAH ratios (< 1) and the strong correlation between them ($r > 0.92$; $P < 0.001$) but also is also supported by a series of individual and

group PAH ratios. For instance, a ratio $FLA/(FLA+PYR) < 0.4$ typically defines petroleum contamination (Baumard et al. 1999); however, most of the sampling stations of all three marinas ratios fell in the range $0.4 < FLA/(FLA+PYR) < 0.5$ suggesting petroleum combustion. However, some samples had ratios exceeding 0.5, suggesting PAHs are also from coal and biomass combustion, as shown in a series of double –ratio cross plots (Fig. 7). Furthermore, because BaP is typically nearly negligible in petroleum, it has been considered to be a marker for combustion-derived PAHs (Magi et al. 2002). In the present study, there was a highly significant correlation between BaP and parent PAHs-BaP ($r = 0.95$; $P < 0.001$), strongly supporting the predominantly pyrogenic origin of the PAH in marina sediments.

Combustion sources appear to be the main origin of the PAHs found in marinas. The role of docked recreational boats in sediment PAH pollution seems to be secondary, relative to external inputs from stormwater runoff from land, although boating-associated activities (e.g. boat cleaning, fueling operations), boat motor exhaust and occasional spills may contribute to PAH accumulation in marina sediments (Fairey et al. 1998; Yılmaz et al. 2014). In effect, the SDB spatial distribution of sediment PAH concentrations is not associated with boat presence as is the case for copper, where clear gradients were observed (Neira et al. 2009; 2014). The predominance of parent PAHs (over 96% of the total PAHs) further supports the pyrogenic origin of PAHs in SDB marinas.

Urban runoff is comprised of wet weather flow (runoff from precipitation events) and dry weather flow (e.g. from irrigation runoff, car washing activities) (US EPA 1983). It is known that storm water runoff and outfalls carry substantial amounts of pollutants

into the marina (US EPA 2001) and off-site upland residential and urban areas carry pollutants into estuarine and coastal environments (Menzie et al. 2002), bays (Schiff and Stevenson 1996) and marina basins (US EPA 2001). Shipbuilding and maintenance activity, as well as storm drains and creek runoff have been mentioned in early studies as major contributors of contamination in SDB (McCain et al. 1992; Stein et al. 2006). Streets and parking lot deposits in surrounding areas also constitute a stock of PAHs in coastal urbanized environments (Ashley and Baker 1999; Mahler et al. 2014; McIntyre et al. 2016). Early studies on sources of PAHs to surface sediments of SDB showed that sediments were largely impacted by pyrogenic PAHs from urban sources, and not by petrogenic PAHs from oil spills (Zeng and Vista 1997).

Motor vehicles are considered a major source of potential carcinogenic HPAHs such as BaP, BaA, and BbKf, particularly in urban areas (Dickhut et al. 2000). This is in line with other studies that indicate that a major source of PAHs in urban areas is surface water runoff (Hoffman et al. 1984; Exponent 2003; Motelay-Massei 2006), as well as aerial particle deposition, unintended spills, and exhaust dust from combustion motors (Zeng and Vista 1997; Marr et al. 1999). PAHs derived from combustion sources may actually be deposited in the marine water already adsorbed onto atmospheric particulates, such as soot particles (Webster et al. 2009). It has been estimated that 36% of the PAH input into the aquatic environment is due to urban runoff and 71% of this contribution is composed of HPAHs (Hoffman et al. 1984). Further studies are necessary to evaluate and elucidate the relative contribution of specific potential local sources of PAHs in SDB marinas.

Conclusion

The present study provides valuable baseline information on actual levels of PAHs in sediments at a high spatial-resolution of concentration distributions across SDB marinas. Although the marinas studied are small in size relative to SDB as a whole, the high-spatial resolution sampling design applied revealed patterns of PAH distribution unrelated to moored boat presence, and more associated with runoff draining directly to the basin. The toxic unit values in all stations of SIYB were below 1.0 and thus sediment would be considered of low risk for benthic animals (Class A). In contrast, 7 stations of HW and one station of HE presented values above 1.0 suggesting sediments to be potentially toxic (Class B). Parent PAHs accounted for over 96% of the total PAHs targeted in this study, where high molecular weight PAHs (4-6 rings) were dominant (>86%), suggesting largely a pyrogenic origin of PAHs found in marina sediments. The fraction of carcinogenic PAHs was high at all sites (61-70%) where BaP contributed over 90% to the BaP toxic equivalents (BaP-TEQ). This raises concerns about potential impact on sediment-dwelling faunal communities and ecosystem-level consequences. The information provided here can help city and waterways managers and regulators to localize areas of possible environmental health impacts in the studied marinas, assess future threats to sediment quality, and facilitate the evaluation of management options. Mitigation measures for parking lots and streets such as natural treatment systems (biofilters, rain garden, permeable pavement (e.g. Wright et al. 2009; Grant et al. 2012; Askarizadeh et al. 2015; McIntyre et al. 2016) could effectively reduce input of PAHs and other pollutants to the basins.

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