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Baseline

Polychlorinated biphenyls (PCBs) in recreational marina sediments of San Diego Bay, southern California

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ABSTRACT

Polychlorinated biphenyl (PCB) concentrations were determined in surface sediments from three recreational marinas in San Diego Bay, California. Total PCB concentrations ranged from 23 to 153, 31–294, and 151–1387 ng g^{-1} for Shelter Island Yacht Basin (SIYB), Harbor Island West (HW) and Harbor Island East (HE), respectively. PCB concentrations were significantly higher in HE and PCB group composition differed relative to HW and SIYB, which were not significantly different from each other in concentration or group composition. In marina sediments there was a predominance (82–85%) of heavier molecular weight PCBs with homologous groups (6CL-7CL) comprising 59% of the total. In HE 75% of the sites exceeded the effect range median (ERM), and toxicity equivalence (TEQ dioxin-like PCBs) values were higher relative to those of HW and SIYB, suggesting a potential ecotoxicological risk.

There is increasing concern about environmental pollution of coastal areas, bays and marina basins due to contamination with organic pollutants such as polychlorinated biphenyls (U.S. EPA, 2001). PCBs are a class of man-made aromatic compounds consisting of carbon, hydrogen and chlorine atoms that have been widely used in capacitors, transformers, electrical equipment, lubricants and coolants by virtue of their electrical insulating properties, chemical stability and low flammability (U.S. EPA, 1999; ATSDR, 2000). PCBs persist in practically all types of environments worldwide, and frequently at remarkably high levels (Häggblom and Bossert, 2003; Wong et al., 2009; Pozo et al., 2007; Fuoco et al., 2009; EEA, 2011; Hutchinson et al., 2013). Their persistence, stability, long-range transport, bioaccumulation and biomagnification ability, as well as toxicity to aquatic life and potential carcinogenicity to higher organisms (Smith et al., 1999; Persky et al., 2001; Weintraub and Birnbaum, 2008; ATSDR, 2000, 2011; Su et al., 2014) arise from features such as halogenation, low vapor pressure (low volatility) and high hydrophobicity (Nicklisch et al., 2016).

San Diego Bay (SDB) is an important water body in southern California due to its ecological value and because it supports tourism, commerce, recreation and fishing, as well as a variety of industrial and military uses. At the same time SDB is an end point for waters from adjacent urbanized and industrialized areas as well as watersheds, and as such, it is especially vulnerable to pollution. SDB has been listed as an impaired water body, and ranked as one of the most contaminated urbanized areas in the country (O'Connor, 1990; McCain et al., 1992; Fairey et al., 1996, 1998; Bay et al., 2016). SDB sediments containing absorbed contaminants have been considered a local source of PCBs, not only for bay benthic organisms, but also for offshore shelf sediments and fish via ocean outfall and dumping of dredged sediments from SDB (Zeng et al., 1998; Parnell et al., 2008; RWQCB, 2017).

Despite the high number of hazardous compounds contaminating the marine environment, information with sufficient spatial coverage to identify hotspots of contamination or to enable appropriate assessment in relation to sources and local effects is lacking (Pozo et al., 2009; Hedge et al., 2017). Most studies and monitoring programs in SDB measuring pollutants have focused on bay-wide analyses (e.g. Fairey et al., 1996, 1998; Noblet et al., 2003; Blake et al., 2004; Schiff et al., 2016). However, recent studies in small marinas have documented the importance of identifying the small spatial scales (ten of meters) at which contaminants such as PAHs and copper can disperse in sediments and act on benthic faunal communities in small marinas (Neira et al., 2009, 2011, 2014, 2015, 2017).

The present study provides an overview of the actual levels of PCBs in surficial sediments of three SDB recreational marinas. Specifically we address the following questions, (1) What are the concentrations of PCBs in superficial sediments? (2) How are PCBs spatially distributed? (3) How do PCB congener and PCB homolog compositions differ among marinas? (4) Are there trends and hotspots of PCB concentration associated with key environmental parameters (e.g. TOC, mud,

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Fig. 1. Location of the study area in the north section of San Diego Bay, California showing sampling sites in (A) Shelter Island Yacht Basin, (B) Harbor Island West, and (C) Harbor Island East.

phytopigments)? (5) Do PCB levels pose a potential risk to aquatic organisms? and (6) How do PCB levels in SDB marina sediments compare to those in other local, national, and worldwide studies? We offer the null hypothesis that due to proximity of the three marinas studied, no major differences in PCB concentrations and composition will be observed.

Study sites were located in the north section of SDB (32°40′ N, 117°4′W) and included three marina basins, Shelter Island Yacht Basin (SIYB), Harbor Island West (HW) and Harbor Island East (HE) (Fig. 1). The north and central portion of SDB is greatly influenced by the Pueblo watershed of about 155 km^2, an area highly urbanized (~500,000 people) which drains through creeks, concrete-lined channels and pipe outfalls directly into SDB (http://www.sdbay.sdsu.edu/education/pueblo.php). All three marinas have relatively well-flushed mouths but restricted water mixing at the heads (Largier, 1995; Chadwick and Largier, 1999). Water residence times along the main channel are estimated to be 5–6 days for SIYB, and 6–8 and 8–11 days for HW and HE, respectively (Chadwick et al., 2004; F. Maicu/A. Zirino, pers. comm). Further details of the study locations are reported in Neira et al. (2009, 2011, 2014).

Twenty stations in SIYB, 14 in HW and 8 in HE, covering the whole basin spanning moored boat areas and open water areas, were sampled from a small boat (July 2014) (Fig. 1). Sediment samples (0–5 cm depth, 20.4 cm^2 surface area) were collected and processed as described previously by Neira et al. (2017).

Target analytes were 26 PCB congeners C-WNN 10 μg mL^{-1} as the PCB standards, comprising the PCB congeners 8, 18, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 169, 170, 180, 187, 189, 196, 206, and 209 (AccuStandard, New Haven, CT, USA). PCB characterization was achieved with Pegasus 4D comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC/TOF-MS) (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. Chromatographic separation was performed by using analytical columns Rtx-5MS (Restek, Bellefonte, PA, USA) with a length of 35 m, and ID of 250 μm and a film thickness of 0.25 μm (Column 1) integrated with a 5-m guard column and Rxi-17 (0.79 m × 100 um × 1 μm). The temperature program for Dimension 1 was initial 60 °C (held for 1 min) at 6 °C min^{-1}, to 300 °C (held for 3 min) at 20 °C min^{-1}, until 320 °C for 15 min. Temperature for Dimension 2 was initial at 85 °C for 1 min at 6 °C min^{-1} until 320 °C for 3 min at 20 °C min^{-1} until 340 °C held for 15 min. Helium was used as a carrier gas at a constant flow of 1 mL min^{-1}, and a volume of 2 μL was injected to GC in splitless at 300 °C. The average limit of detection was 1.64 ng g^{-1}. Concentration of PCBs in sediment is reported in ng g^{-1} on a dry weight basis.

Quality control during extraction, clean-up and analysis procedures was assured by regular analysis of procedural blanks. Quality control procedures included analysis of sample blanks and matrix-spiked samples. For QC, internal $^{13}C_{12}$-PCB 169 (3,3′4,4′5,5′-hexachloro[$^{13}C_{12}$] biphenyl); recovery $^{13}C_{12}$-PCB 189 (2,3,3′,4,4′,5,5′-heptachloro[$^{13}C_{12}$] biphenyl) (Wellington laboratories, Guelph, Canada). Estimates of recoveries for each analysis averaged 55% ± 15%. Calibration standard solutions were analyzed at the beginning, middle and end of each set of