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

Carlos Neira [a, *], Melissa Vales [b], Guillermo Mendoza [a], Eunha Hoh [b] & Lisa A. Levin [a]

[a] Integrative Oceanography Division and Center for Marine Biodiversity and Conservation, Scripps Institution of Oceanography, La Jolla, CA, USA

[b] Graduate School of Public Health, San Diego State University, San Diego, CA, USA

ABSTRACT

Polychlorinated biphenyl (PCB) concentrations were determined in surface sediments from three recreational marinas in San Diego Bay, California. Total PCB concentrations ranged from 23–153, 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.

Keywords: PCB pollution; sediment contamination; spatial distribution; marina; San Diego Bay; California

---

* Corresponding author.

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

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 et al., 2003; Wong et al. 2003; 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 feat,ures 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, 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 cm2 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 were 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 samples, and a five-point level calibration curve was performed. Analytical software ChromaTOF mass spectrometer data version 4.51.6.0 optimized for Pegasus was used for PCB data analysis. The average limit of detection (LOD) was 1.64 ng g^{-1} (Supplementary material **Table S1**).

Concentration levels of individual compounds were often below the limit of detection (LOD). Because an estimate of these concentrations from other data or use of simplified standard estimations, such as setting <LOD data to zero, half-LOD or LOD, would have led to inaccurate or misleading measurements, we only used values that were >LOD. Correlations among investigated PCBs and environmental variables were performed with the Spearman's rank correlation coefficient. One-way ANOVA was used to test for differences in concentrations of PCBs among marinas. The non-parametric Wilcoxon test was used when data transformation did not meet parametric assumptions of normality and homogeneity of variance. Furthermore, in order to overcome differences in sample size per marina, a series of pairwise

tests were conducted by using permutational ANOVA (PerANOVA), followed by Monte Carlo permutation tests on square root transformed data. Spearman and ANOVA analyses were conducted with JMP Pro 12.0.1 (SAS Institute Inc.). PerANOVA was conducted with the PERMANOVA add-on (Anderson et al. 2008) for Primer v6 (Clarke and Gorley, 2006). Spatial patterns of 6 PCB homologous series (2+3Cl, 4Cl, 5Cl, 6Cl, 7Cl, and 8+9+10Cl) for each marina were examined using principal component analysis (PCA). This allows visualization to detect possible site groupings and PCB homologue composition among the marinas. Similarity percentage (SIMPER) procedure was performed to identify homologous groups and proportional contribution to any differences among marinas. Analyses were performed with Primer v6 software package.

Spatial probability maps of PCBs were produced for each marina, using total PCB concentrations (i.e. sum of PCB congeners in ng g^{-1}) that were interpolated on a regular grid by ordinary point kriging. The method uses a weighted average of the neighboring known points to estimate or predict the values of an unobserved value (Sanders, 2007). Kriging calculations were performed in Matlab 2015 and then mapped using ArcGIS v.10.3.

To examine whether PCB levels in sediments represent a potential biological risk, results of PCB levels in sediment were contrasted with established sediment quality guidelines (SQGs) effects range-low (ERL) and effects range-median (ERM) (Long et al., 1995). Concentrations below the ERL (22.7 ng g^{-1}) rarely result in adverse biological effects. Concentrations equal or above the ERM (180 ng g^{-1}) signal the risk of adverse biological effects. The potential environmental risks of sediment PCBs was assessed based on the concept that all PCBs have some grade of toxicity, but the most hazardous are those called dioxin-like PCBs (DL-PCBs). DL-PCBs have a structural similarity with dioxins and can cause toxic responses

similar to those caused by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most potent congener within the persistent halogenated aromatic hydrocarbons (Van den Berg et al., 1998). The toxic mechanism is related to their affinity to bind the aryl hydrocarbon receptor (AHR) (Safe, 1990). Thus, toxicity equivalence (TEQ) values were calculated for each sample by multiplying the individual congener concentration with the corresponding toxic equivalency factor (TEF) established by the World Health Organization (WHO) for humans and fish (Van den Berg et al., 2006) and recommended by the U.S. EPA (2010). TEFs are calculated relative to TCDD, which has an assigned TEF value of 1. For these calculations we only used data based on concentration values >LOD of DL-PCBs. Final results of TEQ for marinas were obtained by summing individual congener concentrations weighted by TEFs (U.S. EPA, 2010). On the other hand, non dioxin-like PCBs (most commonly reported IUPAC #s 28, 52,101, 138, 153, and 180) have been assessed as marker PCBs (M-PCBs) for their ubiquity and frequency of availability. They exhibit other toxic behaviors (e.g. neurotoxic, immunotoxic) than the DL-PCBs, not involving AHR binding (Giesy and Kannan, 1998).

Sediment physicochemical properties include TOC, TN, % mud, phytopigments, and water content (**Table 1)**. TOC and mud content ranged from 0.38% - 1.65%, and 19.7% - 99.2%, respectively. Phytopigments (sum of chl *a* and phaeopigments) were 32.2 μg g^{-1} to 95.2 μg g^{-1}, and water content ranged from 27.1 to 99.2%.

The concentration of the PCBs quantified (sum of 24 congeners) in surface sediments of SDB craft harbors are presented in **Table 2** and Supplementary material **Tables S2, S3 and S4** for SIYB, HW and HE, respectively. Mean (±1SE) total PCB concentrations were 79 ± 9 ng g^{-1} for SIYB, 101 ± 18 ng g^{-1} for HW, and 421 ± 146 ng g^{-1} for HE. The highest PCB concentrations were registered at station HE01 (1387 ng g^{-1}) and station HE02 (551 ng g^{-1}), both

located at the head of the HE basin. Station HE01 is close to a main drainage outfall, where relatively high concentrations of PAHs were also measured (Neira et al. 2017). Total PCB concentrations measured in this study were comparable to those measured by other studies in SDB including a few stations within or adjacent to the study sites (e.g. McCain et al., 1992; Fairey et al., 1996; Stransky et al., 2016), and to those in non-USA sites (**Table 3**).

Maximum concentrations in HE were much higher than other sites in the world and comparable to sites such as Alexandria Harbor (Egypt), Mar Piccolo (Italy) or Great Sound (Bermuda) but lower than Baltimore Harbor, Venice Lagoon, Great Sound Complex (Bermuda) or Naples Harbor (**Table 3**). Direct comparisons with other regions and harbors have to be taken with caution since a suite of factors may influence the results. Sediment properties, for instance (grain size, TOC content) may influence contaminant sorption capacity, congeners present and chlorination degree. Distance from sources (e.g. near industrial, residential, or forested areas), water flushing, and water retention time may also be important (Ashley and Baker, 1999; Davis, 2004; Ouyang et al., 2006).

Total PCB concentrations differed among marinas ($\chi^2 = 17.2$; df = 2; P = 0.0002), being significantly higher in HE than in HW (t = 2.8; P(MC) = 0.009) and SIYB (t = 3.7; P(MC) = 0.001) (perANOVA and a Monte Carlo tests). No significant differences in total PCB concentrations occurred between HW and SIYB (t = 1.2; P(MC) = 0.245) (**Fig. 2**). Higher levels of sediment PCBs observed in HE are in accordance with previous observations for the area nearby, with averaged concentrations of ~350 ng g^{-1} relative to HW (~100 ng g^{-1}) and SIYB (~50 ng g^{-1}) (McCain et al., 1992).

Overall, PCB congeners 138, 153 were the most abundant, both comprising about 33% in SIYB of total PCBs, and about 39% in HW and HE (**Table 2**). They were followed in

importance by congeners 170 and 101 in SIYB, congeners 101 and 180 in HW, and congeners 180 and 101 in HE. Due to the close proximity of the studied marinas, with only a few meters between HW and HE and a few kilometers between these and SIYB, one would expect a similar PCB composition in sediments. Overall there is a clear predominance in abundance of heavier molecular weight PCBs (i.e. > PCB#77, Macias-Zamora et al., 2014), with 82% for SIYB, and 85% for HW and HE (**Table 2**). The composition pattern of homologous groups (i.e. 2+3CL, 4CL, 5CL, 5CL, 6CL, 7CL and 8+9+10CL biphenyl PCBs) is shown in **Fig. 3**. There is a predominance of 6CL, that along with 7CL biphenyls, represents over 59% of the total PCB composition. When each homolog group was compared between marinas (perANOVA), significant differences were observed between SIYB and HE and between HW and HE, but not between SIYB and HW (Supplementary material **Table S5**). However, the relative contribution of PCB congeners varies in each marina, with PCB 138 and PCB 153 comprising about 16% of the total in SIYB and about 20% in both HW and HE (**Table 2**). In HW PCBs 123+118 were more abundant relative to SIYB and HE. PCB156 contributed about 2% to the total composition in HE; it was not detected in SIYB and HW (**Table 2**). The occurrence of higher concentrations and greater diversity of PCB congeners in HE sediments, including some not detected in SIYB and HW (e.g. PCB 114, 156), reflects not only the magnitude but also the multiple sources of PCB contamination to which HE was historically exposed from adjacent industrial and airport activities (Zeng et al. 2002; Ninyo and Moore, 2011; CRWQCB, 2014; http://www.hromadka-associates.com/TDY.pdf; (http://docs.sandiego.gov/councilcomm_agendas_attach/2010/NRC_100614_5a.pdf).

PCA ordination biplots (**Fig. 4**) reveal a weak spatial similarity in the pattern of loadings (i.e. PCB homologue composition) relative to scores (station position) for SIYB (**Fig. 4A**) and

HW (**Fig. 4B**). The first principal component (PC1) has negative loadings on 5CL, 6CL and 7CL homolog groups, and explains 46% and 53% of the cumulative variance for SIYB and HW, respectively (Supplementary material **Table S6**). This component has positive loading on heavy 8+9+10CL PCBs for SIYB and HW but also on light 2+3CL PCBs for HW (**Fig. 4A, 4B**). For HE, PC1 accounts for 62% of the total variance (Supplementary material **Table S6**) and has negative loading on 6CL, and heavy 8+9+10CL, while PC2 (17% variance) has negative loading on 7CL PCBs and positive loadings on lighter (2+3CL, 4CL PCBs) and intermediate weight 5CL PCBs (**Fig. 4C**). Furthermore, similarity percentage (SIMPER) analysis based on a resemblance matrix of Euclidean distance confirmed high dissimilarity of SIYB vs HE and HW vs HE, both ~26% dissimilar, where homolog groups 2+3CL and 4CL contributed to ~40% of dissimilarity, while dissimilarity of 4.8% was observed for SIYB vs HW, where 6Cl and 7CL biphenyl homologous groups contributed to ~40% of dissimilarity.

The dissimilarity in PCB homolog composition of HE relative to SIYB and HW suggests that HE has received a more intense input of PCBs historically, most likely from a diverse suite of sources and pathways of PCB contamination. The inputs are influenced by a wide spectrum of factors and processes (e.g. PCB congener hydrophobicity and degradation rate, physical mixing, bioturbation and remobilization, water retention time, tidal flushing and outflow (e.g. Largier, 1995; Zeng et al., 2002; Ouyang et al. 2006; Peng and Zeng, 2007; Zirino et al., 2013).

Sediment properties such as grain size and TOC are usually associated with sediment retention capacity (Grant and Middleton, 1998). In this regard, pooling together all sites targeted in this study yields a weak correlation between total PCBs and sediment TOC (Spearman $r = 0.437$; $P = 0.004$). However, when analyzing each marina separately, differences

between sediment properties and PCB loading emerge. In SIYB, total PCBs and homologue congener classes show a significant positive correlation with TOC, phytopigments and mud (**Table 4**), while this relationship is not observed for HW and HE (**Table 4**). This observation suggests that in SIYB, microalgae and phytodetritus and grazing zooplankton may play a more important role in transporting and transferring particle-adsorbed PCBs, possibly depositing ingested particles in the form of fecal pellets and through colloidal pump complexation mechanisms (Zirino et al., 2013). The highly significant correlation of PCBs with phaeopigments, derivative products of grazing that are more stable than chl *a* (Konat and Kowalewska, 2001) supports this hypothesis.

Due to their lipophilic nature, PCBs preferentially adsorb onto sediments, particularly where these are fine grained and/or contain a high proportion of TOC. However, organic contaminants do not always follow that pattern (e.g. Ashley and Baker, 1999; Tam et al., 2001; Raza et al., 2013). PCB concentrations were not dependent on TOC or fine fractions in HW and HE sediments. This suggests nonequilibrium partitioning, possibly a substantial spatial variability, and differences in sediment organic matter composition, with OM lability exerting a higher role than the total amount of TOC (Landrum and Faust, 1991). In shallow aquatic environments, dissolved, colloidal and particulate organic matter are not only key components for trapping contaminants (complexation capacity) (McCarthy and Zachara, 1989; Delgadillo-Hinojosa et al., 2008; Zirino et al., 2013), but also for transporting them to other sites (Magaritz et al., 1990; Backhus et al., 1993).

Probability maps of spatial distribution of PCB concentration in surface sediments are shown in **Fig. 5**. In SIYB, a slight gradient of increasing PCB concentration toward the head of the basin is observed. The highest concentrations occur at stations SI01, SI02 and SI03, where

there are a busy small craft harbor, runoff outfalls and a fuel station (Neira et al., 2017). HE exhibited a hotspot PCB concentration at the head, decreasing gradually to the mouth of the basin (Fig. 5C). This hotspot (i.e., station HE01 and HE02), is an area where also relatively high concentrations of PAHs occur, which were associated with an important urban runoff outfall (Neira et al. 2017). There is an intriguing PCB hotspot (294 ng g^{-1}) at the HW mouth (station HW11), in an area (basin mouth) of high tidal exchange (Chadwick et al., 2004) as reflected by the low TOC and mud content (**Table 1**). This finding maybe the result of incidental dredging and boating activities, exposure of historical dumping, deposition of resuspended contaminated sediments and stripping processes involving scavenging by particles (Peng et al., 2002; Peng and Zeng, 2007).

Risk assessment of PCBs has largely been considered a difficult task due to the variable composition of PCB residues in diverse environmental compartments. Individual congeners pose distinctive physicochemical properties and biological behaviors that lead to different environmental distributions and toxicity patterns (Giesy and Kannan, 1998). Overall total PCB concentrations were largely above the ERL. None of the sites in SIYB exceeded the ERM (Supplementary material **Table S2**), while in HW only one site (HW11) showed PCB levels higher than the ERM (Supplementary material **Table S3**). In contrast, in HE, 75% of the sites (Supplementary material **Table S4**) exceeded the ERM, suggesting potential toxicity to aquatic organisms. Although this approach has limitations for predicting ecological risks (Wenning et al. 2005), we use this as a first approach for comparative purposes, as it continues to be reported in the literature (e.g. Ashley and Baker, 1999; Wenning et al., 2005).

TEQ DL-PCB values ranged from 0.063 to 0.453 pg g^{-1} for SIYB, 0.081-0.620 pg g^{-1} for HW, and 0.59-3.48 pg g^{-1} for HE. The TEQ values reported here may be underestimated

because they were derived from DL-PCBs and their corresponding TEFs and do not include in a cumulative way other polychlorinated chemicals that act with the same mechanism, i.e. polychlorinated dibenzo dioxins (PCDD) and furans (PCDF) (Vartiainen et al., 1997; Van den Berg et al., 2006; Okay et al., 2009). Even so, they provide valuable information on which marina is more impacted and allow comparisons with other world regions. TEQ values for SIYB and HW were similar (for HE higher) to those reported for the Cantabria coastal region (0.08-0.52 pg g^{-1}), North Sea (0.6-2.8 pg g^{-1}), and Belgian coast (0.06-0.95 pg g^{-1}) (Danis et al., 2006; Gómez-Lavín et al., 2011) and much lower than TEQ reported for a Turkey shipyard (25 pg g^{-1}), the Gulf of Finland (14.2-25 pg g^{-1}) or the proper Baltic Sea (5.56-50 pg g^{-1}) (Vartiainen et al., 1997; Isosaari et al., 2002; Verta et al., 2007; Okay et al., 2014). In general, there are scarce guidelines with respect to specific levels of DL-compounds in sediment to be considered safe or risky to aquatic biota; those originating from different environmental entities may involve a wide threshold range (0.85-20 pg TEQ g^{-1} (CCME, 2002; Evers et al., 1996). Thresholds as restrictive as 0.85 pg g-^{1} have been suggested as SQGs that may represent a risk to aquatic organisms (CCME, 2002). In the present study most of the sites that exhibited values exceeding that threshold were located in HE (Supplementary material **Table S4**). All TEQ values calculated for SIYB (Supplementary material **Table S2**) and HW (Supplementary material **Table S3**) did not exceed the safe level. However, the application of the TEF approach has been suggested to have some limitations and should be used with caution. Laboratory animal and wildlife studies suggest that the predictive value of TEQs for PCBs may be species- and response-dependent due to additive and antagonistic (non-additive) interactions attributed to PCB mixtures (Safe, 1994).

Overall DL-PCBs comprised about 11% of the total studied PCBs, the other ~89% were represented by marker PCBs (62%) and other congeners (27%) (Supplementary material **Tables S2, S3, S4** for SIYB, HW, and HE, respectively). The most representative were 6CL and 7CL-biphenyls congeners PCB 138, PCB 153, and PCB 180. They have been reported to be common compounds in sediments, soils and biological samples for their high degree of chlorination (ATSDR, 2000). The pattern of dominance of these congeners in sediment is in agreement with previous reports for San Francisco Bay (Davis, 2004), Istanbul Strait (Okay et al., 2009), Venice Lagoon (Secco et al., 2005), and the Spanish northern Atlantic coast (Gómez-Lavín et al., 2011).

Early reports indicate that PCBs were abundant on the northeastern side of SDB (Fairey et al., 1998; Noblet et al., 2002; Zeng et al., 2002). Watersheds of the most industrialized areas of San Diego County drain into SDB, which is already contaminated by local inputs (e.g., shipyards, naval stations, abandoned dumpsites, port activities, transportation infrastructure (Parnell et al., 2008). PCBs can still be released into the Bay from poorly maintained waste sites (ATSDR, 2000; Zeng et al., 2002). Remobilization of PCBs from contaminated sediments has been suggested as a source of PCBs in the water column of SDB (McCain et al., 1992; Zeng et al., 2002). Natural processes (e.g. bioturbation, tidal currents, flooding, erosion) and human activities such as dredging, trawling and vessel activities have been reported as mechanisms influencing the fate of PCBs (and other organic contaminants) in SDB (Peng et al., 2002; Peng and Zeng, 2007; Montgomery et al., 2008; Rodenburg et al., 2011; Bradshaw et al., 2012; Barnard et al., 2017).

There is increasing literature reporting that new PCBs are unintentionally generated as by-products of chemical manufacture involving chlorinated compounds (Panero et al., 2005;

Guo et al., 2014). Indeed, recent studies have indicated that PCBs are found as contaminants in pigments and dyes which are used in a wide range of consumer products (Rodenburg et al., 2010; Hu et al., 2010). They also can be generated by incomplete combustion of products containing carbon and chlorine (ATSDR, 2000). Recent work has highlighted that inhalation exposure to PCBs may have been underestimated in terms of human health risks (Lehmann et al., 2015). The high PCB concentrations found in sediments of HE may be associated with an area (Convair Lagoon) located near the mouth of the HE basin and adjacent to SD International Airport that was highly contaminated with PCBs and that was capped with sand and rocks in 1998 (Zeng et al., 2002; Ninyo and Moore, 2011). As a result, one would expect to find high concentrations at stations nearest to Convair Lagoon, e.g. HE08, HE07. Instead these stations had the lowest concentrations relative to the sites toward the head of the basin (Supplementary material **Table S4)**, with a peak at station HE01 and HE02 (**Fig. 5C, Fig. 1**). These results suggest that other (historical) source(s) of PCBs play a role here, for instance surface runoff (Zeng et al., 2002). Coincidently, station HE01 is near a stormwater outfall where PAH levels are also relatively high (Neira et al., 2017). Adjacent to HE and HW is the San Diego International airport whose different activities can produce or release PCBs and other contaminants that may ultimately reach sediments from airport surface runoff waters (Sulej et al., 2011; CRWQCB, 2014).

Results presented here provide information on the current levels of PCBs in SDB marinas and their spatial distribution; such information is relevant for managing urbanized marinas and harbors on a regional and international scale. These data can also be used as a baseline for future monitoring programs. PCBs are only one of many contaminant types that are

present in SDB; metals such as copper, polycyclic aromatic hydrocarbons, and organochlorinated pesticides are others (Neira et al., 2009, 2017; Schiff et al., 2016). In the face of climate and global change (Noyes and Lema, 2015) it is important to have baseline information, especially from understudied coastal urban areas subjected to increased human pressure. Sea level rise and its effects may exacerbate pollution through resuspension and remobilization of otherwise buried contaminated sediments; SDB is not exempt from such changes (CCCC, 2009; NAVFAC, 2013; Gersberg, 2014).

Acknowledgements

Authors thank M. Carter who kindly and safely operated the boat and provided assistance during the field work. We also appreciate the assistance in the laboratory provided by J. Fumo, J. Gonzalez, and K. Watanabe. We acknowledge R. Lee (WSU) for TOC measurements. We are grateful to A. Mehring for valuable comments on an early version of the manuscript, and C. Stransky for providing relevant data and reports. We appreciate the strong support of R. Flick and V. Matuk for promoting this research in San Diego Bay. This study was funded by the California State Parks Division of Boating and Waterways (Award # C1370011) to CN and LAL.

References

Anderson, M.J., Gorley, R.N., Clarke, K.R. 2008. PERMANOVA+ for PRIMER: Guide to Software and Statistical Methods. PRIMER-E, Plymouth, UK.

ATSDR (Agency for Toxic Substances and Disease Registry), 2000. Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, 948 pp. (https://www.atsdr.cdc.gov/toxprofiles/tp17.pdf).

ATSDR (Agency for Toxic Substances and Disease Registry), 2011. Addendum to the toxicological profile for polychlorinated biphenyls. Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine. (https://www.atsdr.cdc.gov/toxprofiles/pcbs_addendum.pdf).

Ashley, J.T.F. and Baker, J.E., 1999. Hydrophobic organic contaminants in surficial sediments of Baltimore Harbor: Inventories and sources. Environ. Technol. Chem. 18, 838-849.

Backhus, D.A., Ryan, J.N., Groher, D.M., Macfarlane, J.K., Gschwend, P.M., 1993. Sampling colloids and colloid-associated contaminants in ground water. Groundwater 31, 466-479.

Barakat, A.O., Kim, M., Qian, Y., Wade, T.L., 2002. Organochlorine pesticides and PCBs residues in sediments of Alexandria Harbour, Egypt. Mar. Pollut. Bull. 44, 1421-1434.

Barnard, P.L., Hoover, D., Hubbard, D.M., Snyder, A., Ludka, B.C., Allan, J., Kaminsky, G.M., Ruggiero, P., Gallien, T.W., Gabel, L., McCandless, D., Weiner, H.M., Cohn, N., Anderson, D.L., Serafin, K.A., 2017. Extreme oceanographic forcing and coastal response due to the 2015-2016 El Niño. Nat. Commun. 8, 14365, doi: 10.1038/ncomms14365.

Battelle, Blasland, Bouck & Lee, Inc., Neptune & Company, 2005. Hunters Point Shipyard Parcel F Validation Study Final Report. San Francisco Bay, CA, USA. (https://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/3dc283e6c5d6056f88257426007417a2/a77b7fb5b4fa6ccb8825799c00788424/$FILE/Hunters%20Point%20Final%20Validation%20Study%20Parcel%20F%20-%20Main%20Contents%20-%205-2-05.pdf).

Bay, S.M., Greenstein, D.J., Parks, A.N., Zeeman, C.Q.T., 2016. Assessment of Bioaccumulation in San Diego Bay. Southern California Coastal Water Research Project, SCCWRP Technical Report 953. (http://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/953_SDBay_Bioaccum.pdf).

Blake, A.C, Chadwick, D.B., Zirino, A., Rivera-Duarte, I., 2004. Spatial and temporal variations in copper speciation in San Diego Bay. Estuaries 27, 437-447.

Bradshaw, C., Tjensvoll, I., Sköld, M., Allan, I.J., Molvaer, J., Magnusson, J., Naes, K., Nilsson, H.C., 2016. Bottom trawling resuspends sediment and releases bioavailable contaminants in a polluted fjord. Environ. Pollut. 170, 232-241.

CCCC (California Climate Change Center), 2009. Climate Change-Related Impacts in the San Diego Region by 2050. CEC-500-2009-027-F. (http://www.energy.ca.gov/2009publications/CEC-500-2009-027/CEC-500-2009-027-F.PDF).

Cardellicchio, N., Buccolieri, A., Giandomenico, S., Lopez, L., Pizzulli, F., Spada, L., 2007. Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). Mar. Pollut. Bull. 55, 451-458.

CCME (Canadian Council of Ministers of the Environment), 2002. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Summary Tables. Winnipeg: CCME.

Chadwick, D.B., Largier, J.L., 1999. Tidal exchange at the bay-ocean boundary. J. Geophys. Res. 104 (C12), 29, 901-29,924.

Chadwick, D.B., Zirino, A., Rivera-Duarte, I., Katz, C.N., Blake, A.C., 2004. Modeling the mass balance and fate of copper in San Diego Bay. Limnol. Oceanogr. 49, 355-366.

Clarke, K.R., Gorley, R.N., 2006. Primer V6: User Manual/Tutorial. Primer-E, Plymouth.

CRWQCB (California Regional water Quality Control Board) 2014. Laurel Hawthorn Central Embayment, Investigative Order No. R9-2014-0007. (https://www.waterboards.ca.gov/sandiego/board_decisions/adopted_orders/2014/R9-2014-0007.pdf).

Danis, B., Debacker, V., Miranda, C.T., Dubois, Ph., 2006. Levels and effects of PCDD/Fs and co-PCBs in sediments, mussels, and sea stars of the intertidal in the southern North Sea and the English Channel. Ecotoxicol. Environ. Safety 65, 188-200.

Davis, J.A., 2004. The long-term fate of PCBs in San Francisco Bay. Environ. Toxicol. Chem. 23, 2396-2409.

Delgadillo-Hinojosa, F., Zirino, A., Nasci, C., 2008. Copper complexation capacity in surface waters of the Venice Lagoon. Mar. Environ. Res. 66, 404–411.

EEA (European Environment Agency), 2011. Hazardous Substances in Europe's Fresh and Marine Waters. European Environment Agency, Technical Report No 8/2011, Copenhagen, 61 pp.

Evers, E.H.G., Laane, R.W.P.M., Groeneveld, G.J.J., Olie, K., 1996. Levels, temporal trends and risk of dioxins and related compounds in the Dutch aquatic environment. Organohalogen Compd. 28, 117-122.

Fairey, R., Bretz, C., Lamerdin, S., Hunt, J., Anderson, B., Tudor, S., Wilson, C.J., LaCaro, F., Stephenson, M., Puckett, M., Long, E.R., 1996. Chemistry, toxicology, and benthic community conditions in sediments of the San Diego Bay region. Final Report. California State Water Resources Control Board, Sacramento, CA. (http://www.waterboards.ca.gov/water_issues/programs/bptcp/docs/reg9report.pdf).

Fairey, R., Roberts, C., Jacobi, M., Lamerdin, S., Clark, R., Downing, J., Long, E., Hunt, J., Anderson, B., Newman, J., Tjeerdema, R., Stephenson, M., Wilson, C., 1998. Assessment of sediment toxicity and chemical concentrations in the San Diego Bay region, California, USA. Environ. Toxicol. Chem. 17, 1570-1581.

Frignani, M., Belluci, L.G., Carraro, C., Raccanelli, S., 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon. Chemosphere 43, 567-575.

Fuoco, R., Giannarelli, S., Wei, Y., Ceccarini, A., Abete, C., Francesconi, S., Termine, M., 2009. Persistent organic pollutants (POPs) at Ross Sea (Antarctica). Microchem. J. 92, 44-48.

Gersberg, R.M., 2014. San Diego Bay Terrain Model. Final Report, San Diego State University Research Foundation. (https://www.portofsandiego.org/document/environment/environmental-committee-fund/progress-reports/5666-san-diego-bay-terrain-modelfinalreport-feb-2014/file.html).

Giesy, J.P., Kannan, K., 1998. Dioxin-like and non-dioxin-like effects of polychlorinated biphenyls (PCBs): Implications for risk assessment. Critical Rev. Toxicol. 28, 511-569.

Gómez-Lavín, S., Gorri, D., Irabien, A., 2011. Assessment of PCDD/Fs and PCBs in sediments from the Spanish northern Atlantic coast. Water Air Soil Pollut. 221, 287-299.

Grant, A., Middleton, R., 1998. Contaminants in sediments: Using a robust regression for grain-size normalization. Estuaries 21, 197-203.

Guo, J., Capozzi, SL., Kraeutler, T.M., Rodenburg, L.A., 2014. Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments. Environ. Sci. Technol. 48, 8573-8580.

Häggblom, M.M., Bossert, I.D., 2003. Halogenated organic compounds: a global perspective. In: Häggblom, M.M., Bossert, I.D. (Eds.), Dehalogenation: Microbial Processes and Environmental Applications. New York, NY: Kluwer Academic Publishers, pp. 3–29.

Hedge, L.H., Dafforn, K.A., Simpson, S.L., Johnston, E.L., 2017. Uncovering hidden heterogeneity: Geo-statistical models illuminate the fine scale effects of boating infrastructure on sediment characteristics and contaminants. Mar. Pollut. Bull. 119, 143-150.

Hu, D., Hornbuckle, K.C., 2010. Inadvertent polychlorinated biphenyls in commercial paint pigments. Environ. Sci. Technol. 44, 2822-2827.

Hutchinson, T.H., Lyons, B.P., Thain, J.E., Law, R.J., 2013. Evaluating legacy contaminants and emerging chemicals in marine environments using adverse outcome pathways and biological effects-directed analysis. Mar. Pollut. Bull. 74, 517-525.

Isosaari, P., Kankaampaa, H., Mattila, J., Kiviranta, H., Verta, M., Salo, S.A., Vartiainen, T., 2002. Spatial distribution and temporal accumulation of polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in the Gulf of Finland. Environ. Sci. Technol. 36, 2560-2565.

Jones, R.J., 2011. Spatial patterns of chemical contamination (metals, PAHs, PCBs, PCDDs/PCDFS) in sediments of a non-industrialized but densely populated coral atoll/small island state (Bermuda). Mar. Pollut. Bull. 62, 1362-1376.

Konat, J., Kowalewska, G., 2001. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea – trends and fate. Sci. Total Environ. 280, 1-15.

Landrum, P.F., Faust, W.R., 1991. Effect of variation in sediment composition on the uptake rate coefficient for selected PCB and PAH congeners by the amphipod *Diporeia* sp. In:

Mayes, M.A. and Barron, G. (Eds.), Aquatic Toxicology and Risk Assessment: Fourteen Volume, ASTM STP 1124, American Society for Testing and Materials, pp. 263-279.

Largier, J.L., 1995. San Diego Bay Circulation: A study of the circulation of water in San Diego Bay for the purpose of assessing monitoring and managing the transport and potential accumulation of pollutants and sediment in San Diego Bay. The California State Water Resources Control Board and the California Regional Water Quality Control Board, San Diego Region, San Diego.

Lehman, G.M., Christensen, K., Maddaloni, M., Phillips, L.J., 2015. Evaluating health risks from inhaled polychlorinated biphenyls: research needs for addressing uncertainty. Environ. Health Perspect. 123, 109-113.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19, 81-97.

Macías-Zamora, V., Ramírez-Álvarez, J.L., Sanchez-Osorio, J.L., 2014. A decadal trend study (1998-2008) of POPs in marine sediments at the south of the Southern California Bight. Sci. Total Environ. 491-492, 205-211.

Magaritz, M., Ameil, A.J., Ronen, D., Wells, M.C., 1990. Distribution of metals in a polluted aquifer: A comparison of aquifer suspended material to fine sediments of the adjacent environment. J. Contam. Hydrol. 5, 333-347.

McCain, B.B., Chan, S.-L., Krahn, M.M., Brown, D.W., Myers, M.S., Landahl, J.T., Oierce, S., Clark, Jr. R.C., Varanasi, U., 1992. Chemical contamination and associated fish diseases in San Diego Bay. Environ. Sci. Technol. 26, 725-733.

McCarthy, J.F., Zachara, J.M., 1989. Subsurface transport of contaminants. Environ. Sci. Technol. 23, 496-502.

Mohammed, A., Peterman, P., Echols, K., Feltz, K., Tegerdine, G., Manoo, A. Maraj, D., Agard, J., Orazio, C., 2011. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbor sediments from Sea Lots, Pot-of-Spain, Trinidad and Tobago. Mar. Pollut. Bull. 62, 2324-1332.

Montgomery, M.T., Osburn, C.L., Furukawa, Y., Gieskes, J.M., 2008. Increased capacity for polycyclic aromatic hydrocarbon mineralization in bioirrigated coastal marine sediments. Bioremediat. J. 12, 98-110.

Nakanishi, K. 1996. Hydrophobic organic contaminants in sediments of the Chesapeake Bay. MS thesis. University of Maryland, College Park, MD, USA.

NAVFAC (U.S. Department of the Navy, Naval Facilities Engineering Command Southwest and Port of san Diego), 2013. San Diego Bay Integrated Natural Resources Management Plan, Final September 2013. San Diego, California. Prepared by Tierra Data Inc., Escondido, California. (https://www.portofsandiego.org/document/environment/natural-resources/5730-inrmp-september-2013/file.html).

Neira, C., Cossaboon, J., Mendoza, G., Hoh, E., Levin, L.A., 2017. Occurrence and distribution of polycyclic aromatic hydrocarbons in surface sediments of San Diego Bay marinas. Mar. Pollut. Bull. 114, 466-479.

Neira, C., Delgadillo-Hinojosa, F., Zirino, A., Mendoza, G., Levin, L.A., Porrachia, M., Deheyn, D.D., 2009. Spatial distribution of copper in relation to recreational boating in a California shallow-water basin. Chem. Ecol. 25, 1-17.

Neira, C., Levin, L.A., Mendoza, G., Zirino, A., 2014. Alteration of benthic communities associated with copper contamination linked to boat moorings. Mar. Ecol. 35, 46-66.

Neira, C., Mendoza, G., Levin, L.A., Zirino, A., Delgadillo-Hinojosa, F., Porrachia, M., Deheyn, D., 2011. Macrobenthic community response to copper in Shelter Island Yacht Basin, San Diego Bay, California. Mar. Pollut. Bull. 62, 701-717.

Neira, C., Mendoza, G., Porrachia, M., Stransky, C., Levin, L.A., 2015. Macrofaunal recolonization of copper-contaminated sediments in San Diego Bay. Mar. Pollut. Bull. 101, 794-804.

Nicklisch, S.C.T., Rees, S.D., McGrath, A.P., Gökirmak, T., Bonito, L.T., Vermeer, L.M., Cregger, C., Loewen, G., Sandin, S., Chang, G., Hamdoun, A., 2016. Global marine pollutants inhibit P-glycoprotein: Environmental levels, inhibitory effects, and cocrystal structure. Sci. Adv. 2:e1600001.

Ninyo and Moore, 2011. Water Quality Technical Study Shipyard Sediment Alternative Analysis Convair Lagoon, San Diego, California. Geotechnical and Environmental Sciences Consultants, San Diego, California. (http://www.waterboards.ca.gov/sandiego/water_issues/programs/shipyards_sediment/docs/sediment_cleanup/ceqa/updates_061611/ApO.pdf).

Noblet, J.A., Zeng, E.Y., Baird, R., Grossett, R.W., Ozretich, R.J., Phillips, C.R., 2003. Southern California Bight 1998 Regional Monitoring Program: VI. Sediment Chemistry. Southern California Coastal Water Research Project. (http://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/381_bight98chemistry.pdf).

Noyes, P.M., Lema, S.C., 2015. Forecasting the impacts of chemical pollution and climate change interactions on the health of wildlife. Curr. Zool. 61, 669-689.

O'Connor, T.P., 1990. Coastal Environmental Quality in The United States, 1990: Chemical Contamination in Sediment and Tissues. A Special NOAA 20th Aniversary Report. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Oceanic Service, Rockville, MD.

Okay, O.S., Karacik, B., Basak, S., Henkelmann, B., Bernhoft, S., Schramm, K.W., 2009. PCB and PCDD/F in sediments and mussels of the Istambul strait (Turkey). Chemosphere 76, 159-166.

Okay, O.S., Karacik, B., Güngördü, A., Ozmen, Yilmaz, A., Koyunbaba, N.C., Yakan, S.D., Korkmaz, V., Henkelman, B., Schramm, K.-W., 2014. Micro-organic pollutants and biological response of musserl in marinas and ship building/breaking yards in Turkey. Sci. Total Environ. 496, 165-178.

Ouyang, Y., Zhang, J.E., Ou, L.-T., 2006. Temporal and spatial distributions of sediment total organic carbon in an estuary river. J. Environ. Qual. 35, 93-100.

Panero, M., Boehme, S., Muñoz, G., 2005. Pollution Prevention and Management Strategies for Polychlorinated Biphenyls in the New York/New Jersey Harbor. New York Academy of Sciences, New York. (http://www.nyas.org/WhatWeDo/Harbor.aspx).

Parnell, P.E., Groce, A.K., Stebbins, T.D., Dayton, P.K., 2008. Discriminating sources of PCB contamination in fish on the coastal shelf off San Diego, California (USA). Mar. Pollut. Bull. 56, 1992-2002.

Peng, J., Zeng, E.Y., 2007. An integrated geochemical and hydrodynamic model for tidal coastal environments. Mar. Chem. 103, 15-29.

Peng, J., Zeng, E.Y., Ku, T.-L., Luo, S., 2002. Significance of sediment resuspension and tidal exchange to reduction of polychlorinated biphenyl mass in San Diego Bay, California. Southern California Coastal Water Research Project, 2001-2002 Annual Report, pp.101-109. (http://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2001_02AnnualReport/10_ar12-eddy.pdf).

Persky, V., Turyk, M., Anderson, H.A., Hanrahan, L,P., Falk, C. Steenport, D.N. Chatterton, R. Jr, Freels, S., Consortium, G.L., 2001. The effects of PCB exposure and fish consumption on endogenous hormones. Environ. Health Perspect. 109, 1275-1283.

Pozo, K., Urrutia, R., Barra, R., Mariottini, M., Treutler, H.-C., Araneda, A., Focardi, S., 2007. Records of polychlorinated biphenyls (PCBs) in sediments of four remote Chilean Andean Lakes. Chemosphere 66, 1911-1921.

Pozo, K., Lazzerini, D., Perra, G., Volpi, V., Corsolini, S., Focardi, S., 2009. Levels and spatial distribution of polychlorinated biphenyls (PCBs) in superficial sediment from 15 Italian Marine Protected Areas (MPA). Mar. Pollut Bull. 58, 765-786

Raza, M., Zakaria, M.P., Hashim, N.R., Yim, U.H., Kannan, N., Ha, S.Y., 2013. Composition and source identification of polycyclic aromatic hydrocarbons in mangrove sediments of peninsular Malaysia: indication of anthropogenic input. Environ. Earth Sci. 70, 2425-2436.

Rodenburg, L.A., Guo, J., Du, S., Cavallo, G.J., 2010. Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenil (PCB11). Environ. Sci. Technol. 44, 2813-2821.

Rodenburg, L.A., Songyan, D., Xiao, B., Fennell, D.E., 2011. Source apportionment of polychlorinated biphenyls in the New York/New Jersey Harbor. Chemosphere 83, 792-798.

RWQCB (Regional Water Quality Control Board), 2017. Assessing contaminants in fish & shellfish in San Diego Bay. Monitoring & Assessment, San Diego Water Board. (https://www.waterboards.ca.gov/sandiego/press_room/community_outreach/docs/FSC_statusSheet_FINAL.pdf).

Safe, S., 1990. Polychlorinated biphenyls (PCBs) dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit. Rev. Toxicol. 21, 51-88.

Safe, S.H., 1994. Polychlorinated biphenyls (PCBs): Environmental impacts, biochemical and toxic responses, and implications for risk assessment. Crit. Rev. Toxicol. 24, 87-149.

Sanders, L. (Ed.), 2007. Models in Spatial Analysis Geographical Information Systems Series. ISTE Ltd, London.

Savinov, V.M., Savinova, T.N., Matishov, G.G., Dahle, S., Naes, K., 2003. Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechanga, Barents Sea, Russia. Sci. Total Environ. 306, 39-56.

Schiff, K., Greenstein, D., Dodder, N., Gillett, D.J., 2016. Southern California Bight regional monitoring. Reg. Stud. Mar. Sci. 4, 34-46.

Secco, T., Pellizzato, F., Sfriso, A., Pavoni, B., 2005. The changing state of contamination in the Lagoon of Venice. Part 1: Organic pollutants. Chemosphere 58, 279-290.

Smith, C.R., Baker, L.F., Jessen-Eller, K., Reinisch, C.L., 1999. Polychlorinated biphenyls (PCBs) selectively disrupt serotonergic cell growth in the developing *Spisula* embryo. Toxicol. Sci. 50, 54-63.

Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbor (southern Italy). Chemosphere 67, 998-1009.

Stransky, C., Sheredy, C., Tait, K., Isham, B., Rudolph, J., Schottle, R., Gibbons, P., Holman, K., Maechler, P., Kolb, R., Gamble, J., Lahhsaiezadeh, M., Goong, S., Peng, J., 2016. Final Regional Harbor Monitoring Program 2013 Report. Amec Foster Wheeler Environment & Infrastructure, Inc. Port of San Diego, Agreement Number: 50-2013, Amec Foster Wheeler Project No. 1315102304.

Su, H., Wu, F., Zhang, R., Zhao, X., Mu, Y., Feng, C., Giesy, J.P., 2014. Toxicity reference values for protecting aquatic birds in China from effects of polychlorinated biphenyls. Rev. Environ. Contam. Toxicol. 230, 59-82.

Sulej, A.M., Polkowska, Z., Namiesnik, J., 2011. Contamination of runoff water at Gdansk Airport (Poland) by polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Sensors 11, 11901-11920.

Tam, N.F., Ke, L., Wang, X.H., Wong, Y.S., 2001. Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. Environ. Pollut. 114, 255-263.

U.S. EPA (Environmental Protection Agency), 1999. Polychlorinated Biphenyls (PCBs) Update: Impact on Fish Advisories. Office of Water 4305, EPA-823-F-99-019. (https://www.purdue.edu/hhs/nutr/fish4health/HealthRisks/PCB.pdf).

U.S. EPA (Environmental Protection Agency), 2001. Workshop Report on theApplication of 2,3,7,8-TCDD Toxicity Equivalence Factors to Fish and Wildlife. Risk Assessment Forum, Washington, DC. EPA/630/R-01/002. (https://cfpub.epa.gov/ncea/raf/pdfs/tefworkshopforum.pdf).

U.S. EPA (Environmental Protection Agency), 2010. Recommended Toxicity Equivalence Factors (TEFs) for Human Health Risk Assessments of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and Dioxin-like Compounds. Risk Assessment Forum, Washington, DC. EPA/600/R-10/005. (https://www.epa.gov/sites/production/files/2013-09/documents/tefs-for-dioxin-epa-00-r-10-005-final.pdf).

Van Ael, E., Covaci, A., Blust, R., Bervoets, L., 2012. Persistent organic pollutants in the Scheldt estuary: environmental distribution and bioaccumulation. Environ. Int. 48, 17-27.

Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., et al., 1998. Toxic equivalence factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspect. 106, 775-792.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Petersen, R.E., 2006. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223-241.

Vartiainen, T., Mannio, J., Korhonen, M., Kinnunen, K., Strandman, T., 1997. Levels of PCDD, PCDF and PCB in dated lake sediments in Subarctic Finland. Chemosphere 34, 1341-1350.

Verta, M., Salo, S., Korhonen, M., Assmuth, T., Kiviranta, H., Koistinen, J., Ruokojärvi, P., Isosaari, P., Bergqvist, P.-A., Tysklind, M., Cato, I., Vikelsøe,J., Larsen, M.M., 2007. Dioxin concentrations in sediments of the Baltic Sea - a survey of existing data. Chemosphere 67, 1762-1775.

Weintraub, M., Birnbaum, L.S., 2008. Catfish consumption as a contributor to elevated PCB levels in a non-Hispanic black subpopulation. Environ. Res. 107, 412-417.

Wenning, R.J., Batley, G.E., Ingersoll, C.G., Moore, D.W., 2005. Use of sediment quality guidelines and related tools for the assessment of contaminated sediments. Pensacola, Fl. Society of Environmental Toxicology and Chemistry (SETAC), 815 pp.

Wong, F., Alegria, H.A., Bidleman, T.F., Alvarado, V., Angeles, F., Avila Galarza, A., Bandala, E.R., dela Cerda Hinojosa, I., Galindo Estrada, I., Galindo Reyes, G., Gold-Bouchot, G., Macias Zamora, J.V., Murguía-González, J., Ramirez Espinoza, E., 2009. Passive air sampling of organochlorine pesticides in Mexico. Environ. Sci. Technol. 43, 704-710.

Zeng, E.Y., Yu, C.C., Tran, K., 1998. In-situ measurements of chlorinated hydrocarbons in the water column off the Palos Verdes Peninsula, California. In: Weisberg, S.B., Miller, K.A. (Eds.), Southern California Coastal Water research Project, Westminster, CA.

Zeng, E., Peng, J., Tsukada, D., Ku, T.-L., 2002. In situ measurements of polychlorinated biphenyls in the waters of San Diego Bay. Environ. Sci. Technol. 36, 4975-4980.

Zirino, A., Neira, C., Maicu, F., Levin, L.A., 2013. Comments and implications of steady-state in coastal marine ecosystems. Chem. Ecol. 29, 86-99.

Table 1
Properties of surface sediments (0-5 cm) sampled in Shelter Island Yacht Basin, Harbor Island West and Harbor Island East, San Diego Bay, California. TOC = total organic carbon (% d.w), TN = total nitrogen (% d.w.), Chl *a* = chlorophyll *a* (μg g^{-1} d.w.), Phaeo = phaeopigments (μg g^{-1} d.w); CPE = chloroplastic pigment equivalents (chl *a* + phaeo), Mud (silt/clay) and water content (%).

Site	TOC	TN	Mud	Chl *a*	Phaeo	CPE	Water
		Shelter Island Yacht Basin (SIYB)					
SI01	1.63	0.20	98.4	11.87	70.43	82.30	66.5
SI02	1.07	0.11	72.6	14.91	41.72	56.63	54.0
SI03	1.58	0.19	97.0	15.04	62.11	77.15	64.7
SI04	0.89	0.14	93.0	15.49	42.90	58.39	50.5
SI05	0.49	0.11	32.9	12.74	32.25	44.99	35.4
SI06	1.23	0.17	73.5	3.12	65.71	68.84	52.8
SI07	0.90	0.13	49.0	16.01	56.73	72.74	48.2
SI08	0.69	0.12	55.8	14.92	40.82	55.74	40.0
SI09	0.76	0.11	58.1	16.47	47.81	64.28	45.4
SI10	1.64	0.23	93.1	17.84	61.30	79.14	58.4
SI11	0.92	0.09	80.1	16.16	35.24	51.40	43.8
SI12	0.75	0.11	88.9	18.41	30.81	49.22	48.6
SI13	1.26	0.15	92.6	19.51	62.06	81.57	60.7
SI14	0.52	0.07	77.5	12.78	26.84	39.62	34.3
SI15	0.71	0.12	39.6	22.44	30.15	52.60	38.0
SI16	0.85	0.11	75.1	20.13	48.27	68.40	49.4
SI17	0.38	0.09	20.5	12.98	19.23	32.21	27.1
SI18	0.59	0.09	49.8	17.26	34.29	51.55	35.4
SI19	1.03	0.15	64.4	20.70	60.67	81.36	44.5
SI20	0.42	0.11	19.7	19.16	25.92	45.07	29.0
		Harbor Island West (HW)					
HW01	1.43	0.17	55.7	5.08	81.92	87.00	55.7
HW02	1.57	0.18	97.1	8.69	73.20	81.89	97.1
HW03	1.28	0.17	86.1	17.72	59.31	77.03	86.1
HW04a	1.61	0.17	97.9	8.23	73.15	81.37	97.9
HW05	0.94	0.13	82.9	13.86	49.11	62.97	82.9
HW05a	0.64	0.07	63.1	28.66	44.35	73.01	63.1
HW06	1.65	0.25	99.2	5.29	76.91	82.20	99.2
HW06a	1.54	0.16	86.1	17.57	77.65	95.22	86.1
HW07	0.66	0.09	47.5	15.28	34.45	49.73	47.5
HW08	1.19	0.16	79.7	13.07	61.74	74.81	79.7
HW09	0.52	0.09	51.2	3.48	54.89	58.37	51.2
HW10	0.41	0.10	33.8	15.36	35.40	50.76	33.8
HW11	0.38	0.07	37.2	15.99	33.10	49.10	37.2
HW12	0.48	0.07	30.8	11.75	54.62	66.37	30.8
		Harbor Island East (HE)					
HE01	1.65	0.19	75.8	8.17	45.37	53.54	51.4
HE02	1.30	0.27	68.9	8.94	54.24	63.18	56.1
HE03	0.84	0.17	43.8	12.43	46.73	59.16	46.9
HE04	0.68	0.16	29.6	11.04	32.36	43.40	40.0
HE05	1.23	0.18	67.8	7.71	59.92	67.63	54.7
HE06	0.99	0.16	54.5	14.93	42.81	57.74	45.1
HE07	0.87	0.14	56.9	17.61	51.65	69.26	49.8
HE08	0.52	0.10	52.8	11.12	26.07	37.20	33.7

Table 2
Range of concentrtations (ng g^{-1} d.w.) and relative proportion (%) of PCB congeners in surface sediments of Shelter Island Yacht Basin, Harbor Island West, and Harbor Island East.

	Shelter Island Yach Basin		Harbor Island West		Harbor Island East	
PCB congeners	Range	Relative proportion	Range	Relative proportion	Range	Relative proportion
PCB 8	nd - 2.8	0.5	nd	0	nd - 5.5	0.3
PCB 18	nd - 4.5	1.2	nd	0	1.9 - 16.0	1.2
PCB 28	nd - 6.2	3.2	nd - 13.9	4	5.0 - 23.7	3
PCB 44	nd - 6.0	3.3	nd - 6.7	2.9	3.0 - 41.7	3.2
PCB 52	nd - 8.2	4.1	nd - 9.1	4	1.8 - 9.9	1.9
PCB 66	nd - 10.7	5.7	nd - 27.4	4.6	3.1 - 69.7	5.5
PCB 101	2.2 - 16.4	9.6	2.6 - 26.1	9.8	3.2 - 85.4	8.4
PCB 105	nd - 5.9	4	nd - 16.5	2.9	3.1 - 31.4	4
PCB 114	nd	0	nd	0	nd - 5.5	0.2
PCB 123 + 118	2.1 - 9.2	6.3	2.7 - 21.2	8.1	10.5 - 40. 9	5.8
PCB 138	4.2 - 28.9	17.2	5.5 - 34.1	19.2	21.6 - 143.0	20
PCB 153	3.0 - 27.6	15.4	6.6 - 60.4	21.4	25.8 - 332.5	19
PCB 156	nd	0	nd	0	2.2 - 38.3	1.9
PCB 170	nd - 12.9	9.9	nd - 10.2	5.7	5.4 - 144.1	6
PCB 180	nd - 15.8	9.1	nd - 31.0	9.3	14.0 - 242.9	10.1
PCB 187	2.5 - 13.6	8.3	nd - 22.7	7.9	10.2 - 137.3	7.5
PCB 196	nd	0	nd	0	nd - 22. 2	0.2
PCB 206	nd - 6.3	1.6	nd - 3.08	0.4	nd - 15.8	1.3
PCB 209	nd - 6.0	0.6	nd - 5.2	0.4	nd - 7.6	0.4
Σ light PCBs (<#77)		18		15		15
Σ heavy PCBs (>#77)		82		85		85

nd = no detected

Table 3
Comparison of PCB concentrations (ng g^{-1} d.w.) in sediments of San Diego Bay marinaswith other coastal areas in the world.

Location	PCB range concentration	Mean	References
Venice Lagoon, Italy	6 - 1590		Frignani et al. (2001)
Scheldt Estuary, SE, The Netherlands-Belgium	1.9 - 368	31.5	Van Ael (2012)
Istambul Strait & Marmara Sea, Turkey	0.02 - 540		Okay et al. (2009)
Baltimore Harbor/Patapsco River region, USA	8 - 2150	166	Ashley & Baker (1999)
Chesapeake Bay, USA	0.1 - 62		Nakanishi (1996)
Great Sound Complex, Bermuda	0.5 - 1080		Jones (2011)
Guba Pechanga, Barents Sea, Russia	1.1 - 37.9	12.8	Savinov et al. (2003)
Marina/Shipyard, Mediterranean/NE Aegean Sea, Turkey	0.03 - 139		Okay et al. (2014)
Sea Lots Harbour, Spain	62 - 601		Mohammed et al. 2011
Naples Harbor, Italy	1 - 899	68	Sprovieri et al. (2007)
Mar Piccolo,Taranto, Ionian Sea, southern Italy	2 - 1684		Cardellicchio et al. (2007)
Southern Baltic Sea, Poland	1 - 149	40	Konat & Kowalewska (2001)
Alexandria Harbour, Egypt	0.9 - 1211		Barakat et al. (2002)
San Francisco Bay, USA	nd - 5186		Battelle et al.(2005)
San Diego Bay, USA	0 - 1380		Fairey et al. (1996)
San Diego Bay, Los Angeles/Long Beach Harbor	0 - 412		Noblet et al. (2003)
Marinas (north San Diego Bay)	14 - 411		Stransky et al. (2016)
Shelter Island Yacht Basin, San Diego Bay, USA	23 -153	79	This study
Harbor Island West, San Diego Bay, USA	31 - 294	101	This study
Harbor Island East, San Diego Bay, USA	151 - 1387	421	This study

Table(s) 4

Table 4
Spearman's rank correlation coefficients between total PCBs, PCB homologe congener class based on level of chlorination (2+3 CL, 4 CL, 5 CL , 6 CL, 7 CL, 8+9+10 CL), dioxin-like PCBs (DL-PCBs), marker PCBs (M-PCBs) and sedimentvariables (TOC = total organic carbon, mud content, and phytopigments as chloroplastic pigment equivalents (CPE = sum of chl a and phaeopigments) in Shelter Island Yacht Basin (SIYB), Harbor Island West (HW) and Harbor Island East (HE).

SIYB

Variable	Total PCBs	TOC	Mud	CPE	2+3 CL	4 CL	5 CL	6 CL	7 CL	>8 CL	DL-PCBs	M-PCBs
Total PCBs	-											
TOC	0.683***	-										
Mud	0.567**	0.762***	-									
CPE	0.581**	0.872***	0.565**	-								
2+3 CL	0.699***	0.320	0.199	0.349	-							
4 CL	0.915***	0.539*	0.634**	0.443*	0.629**	-						
5 CL	0.943***	0.683***	0.551*	0.668**	0.601**	0.853***	-					
6 CL	0.947***	0.750***	0.574**	0.699***	0.584**	0.837***	0.948***	-				
7 CL	0.877***	0.660**	0.444*	0.526*	0.573**	0.714***	0.812***	0.804***	-			
>8 CL	0.208	0.145	0.344	-0.079	-0.018	0.365	0.192	0.155	0.259	-		
DL-PCBs	0.917***	0.679**	0.585**	0.656**	0.548*	0.861***	0.980***	0.914***	0.798***	0.257	-	
M-PCBs	0.961***	0.739***	0.555*	0.695***	0.631**	0.859***	0.952***	0.989***	0.818***	0.143	0.920***	-

HW

Variable	Total PCBs	TOC	Mud	CPE	2+3 CL	4 CL	5 CL	6 CL	7 CL	>8 CL	DL-PCBs	M-PCBs
Total PCBs	-											
TOC	0.196	-										
Mud	0.301	0.913***	-									
CPE	0.217	0.855***	0.717**	-								
2+3 CL	0.076	0.428	0.542*	0.229	-							
4 CL	0.735**	-0.044	0.209	-0.112	0.319	-						
5 CL	0.895***	0.323	0.343	0.309	0.021	0.636*	-					
6 CL	0.943***	0.292	0.427	0.186	0.087	0.691**	0.868***	-				
7 CL	0.886***	0.292	0.288	0.389	-0.080	0.444	0.864***	0.815***	-			
>8 CL	-0.184	-0.393	-0.285	-0.238	0.342	0.079	-0.400	-0.346	-0.386	-		
DL-PCBs	0.886***	0.064	0.121	0.077	-0.066	0.715**	0.850***	0.815***	0.811***	-0.238	-	
M-PCBs	0.943***	0.327	0.402	0.309	0.011	0.669**	0.956***	0.943***	0.864***	-0.346	0.828***	-

HE

Variable	Total PCBs	TOC	Mud	CPE	2+3 CL	4 CL	5 CL	6 CL	7 CL	>8 CL	DL-PCBs	M-PCBs
Total PCBs	-											
TOC	0.595	-										
Mud	0.333	0.905**	-									
CPE	-0.119	0.429	0.405	-								
2+3 CL	0.970***	0.539	0.299	-0.252	-							
4 CL	0.809*	0.595	0.452	-0.357	0.814*	-						
5 CL	0.905**	0.405	0.119	0.119	0.874**	0.643	-					
6 CL	0.976***	0.524	0.286	-0.286	0.994***	0.857**	0.881**	-				
7 CL	0.976***	0.548	0.309	-0.095	0.922**	0.738*	0.857**	0.929***	-			
>8 CL	0.814*	0.515	0.419	-0.192	0.831*	0.790*	0.802*	0.850**	0.731*	-		
DL-PCBs	0.928***	0.595	0.405	0.047	0.874**	0.690	0.905**	0.881**	0.905**	0.898**	-	
M-PCBs	1.000***	0.595	0.333	-0.119	0.970***	0.809*	0.905**	0.976***	0.976***	0.814*	0.928***	-

Significance: *$0.01 \le p < 0.05$; **$0.001 \le p < 0.01$; ***$p < 0.001$

Figure Captions

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.

Fig. 2. Box plot showing total PCB concentrations in surface sediments (0-5 cm) of three San Diego Bay marina basins: Shelter Island Yacht basin (SIYB), Harbor Island West (HW), and Harbor Island East (HE). Red plus symbol indicates mean. The central line of the boxplot indicates the median, the box extends from the 25^{th} to the 75^{th} percentiles. Asterisk shows extreme values.

Fig. 3. PCB composition based on the relative abundance (%) of 6 homologous series: ∑di+tri (2+3Cl), tetra (4Cl), penta (5Cl), hexa (6CL), hepta (7Cl), and ∑octa, nona, deca (8+9+10Cl) biphenyls, for (A) Shelter Island Yacht Basin, (B) Harbor Island West, and (C) Harbor Island East.

Fig. 4. Ordination biplots showing results of PCA based on percent composition of six PCB homologous groups in sediment samples, for (A) Shelter Island Yacht Basin, (B) Harbor Island West, and (C) Harbor Island East.

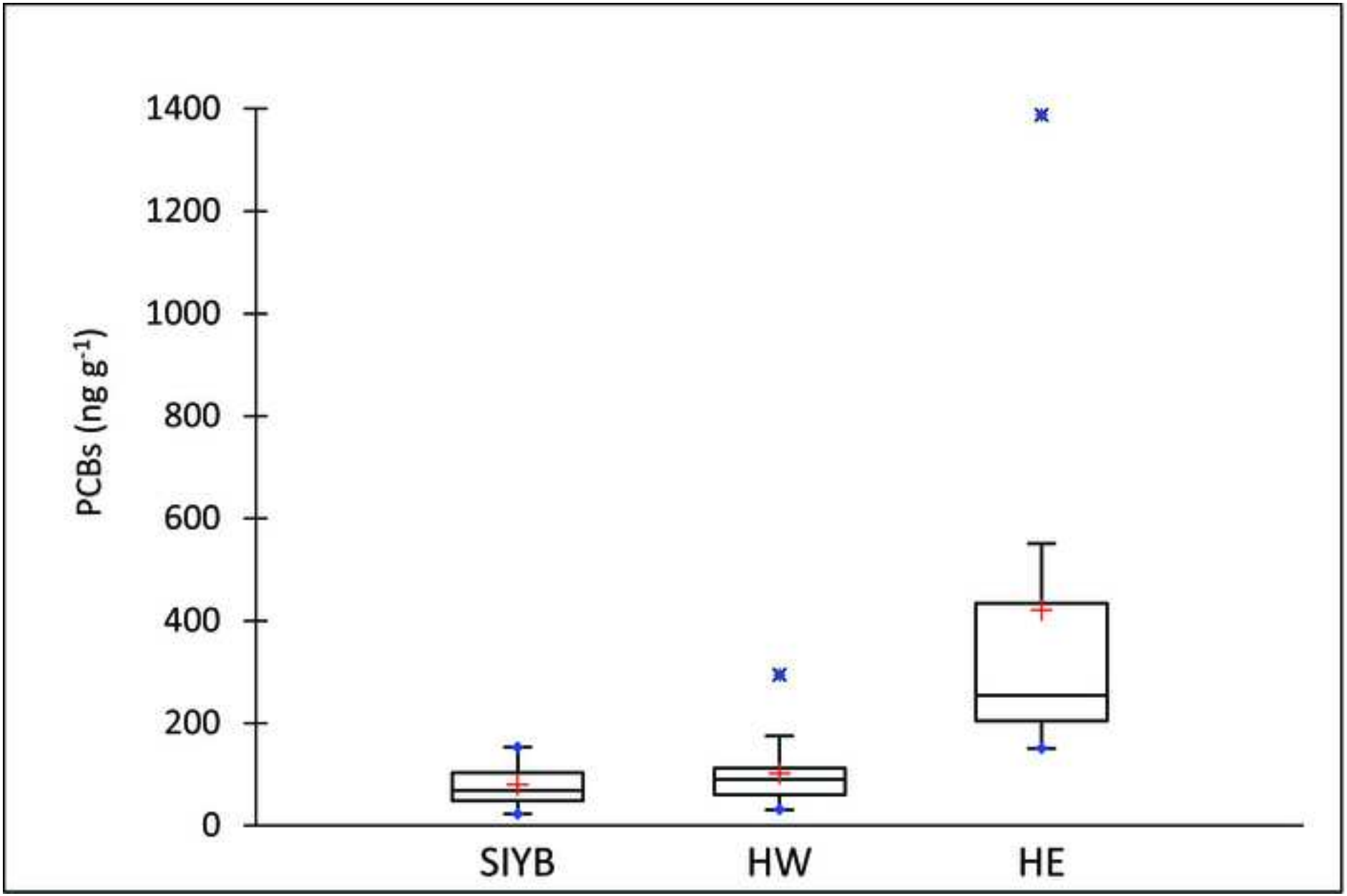
Fig. 5. Probability maps depicting spatial distribution of total PCB concentrations in surface sediments of (A) Shelter Island Yacht Basin, (B) harbor Island West, and (C) Harbor Island East. Note colors are assigned different scale range concentrations (ng g^{-1} d.w.).

Figure(s) 1

Click here to download high resolution image

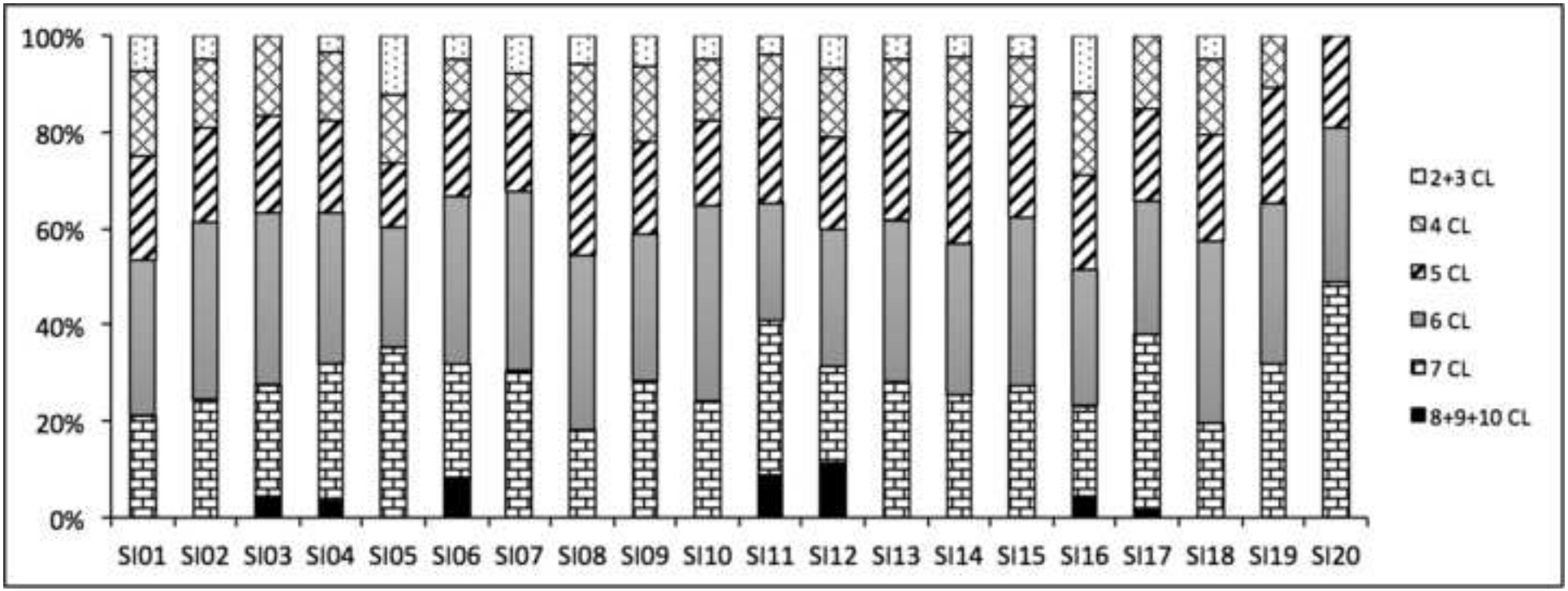
Figure(s) 2

Click here to download high resolution image



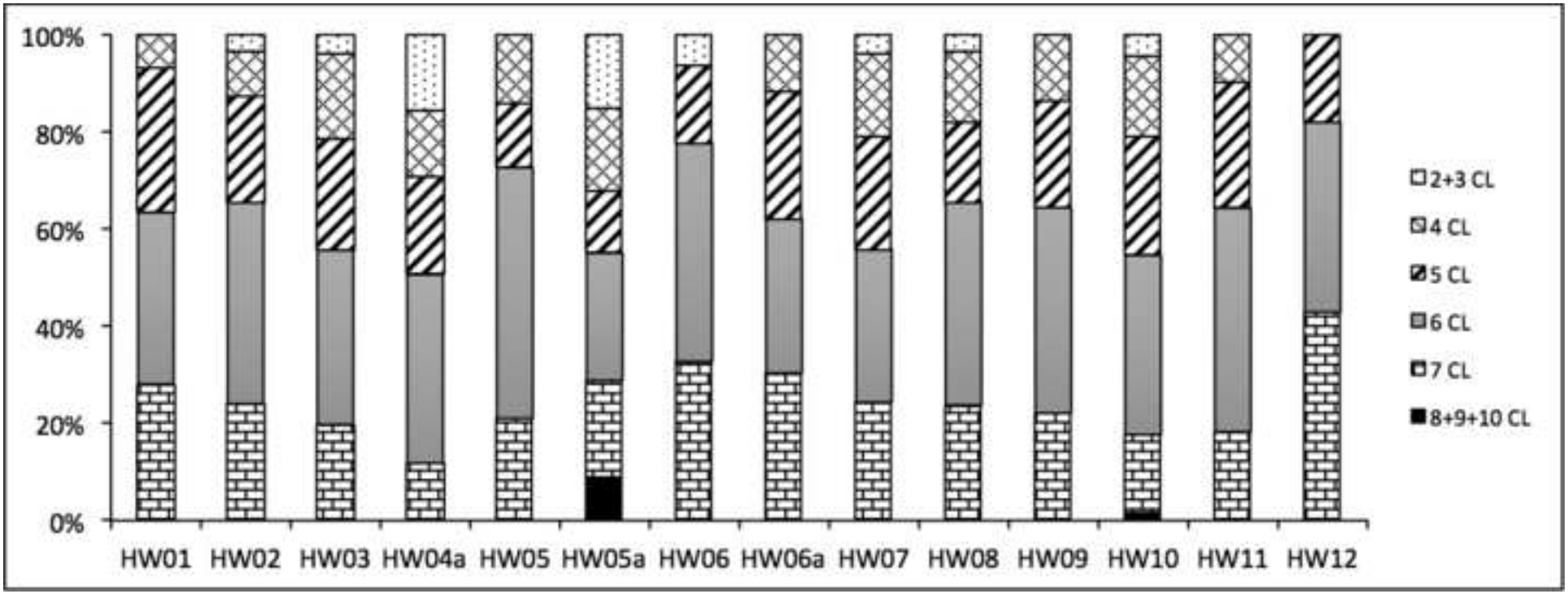
Figure(s) 3A

Click here to download high resolution image



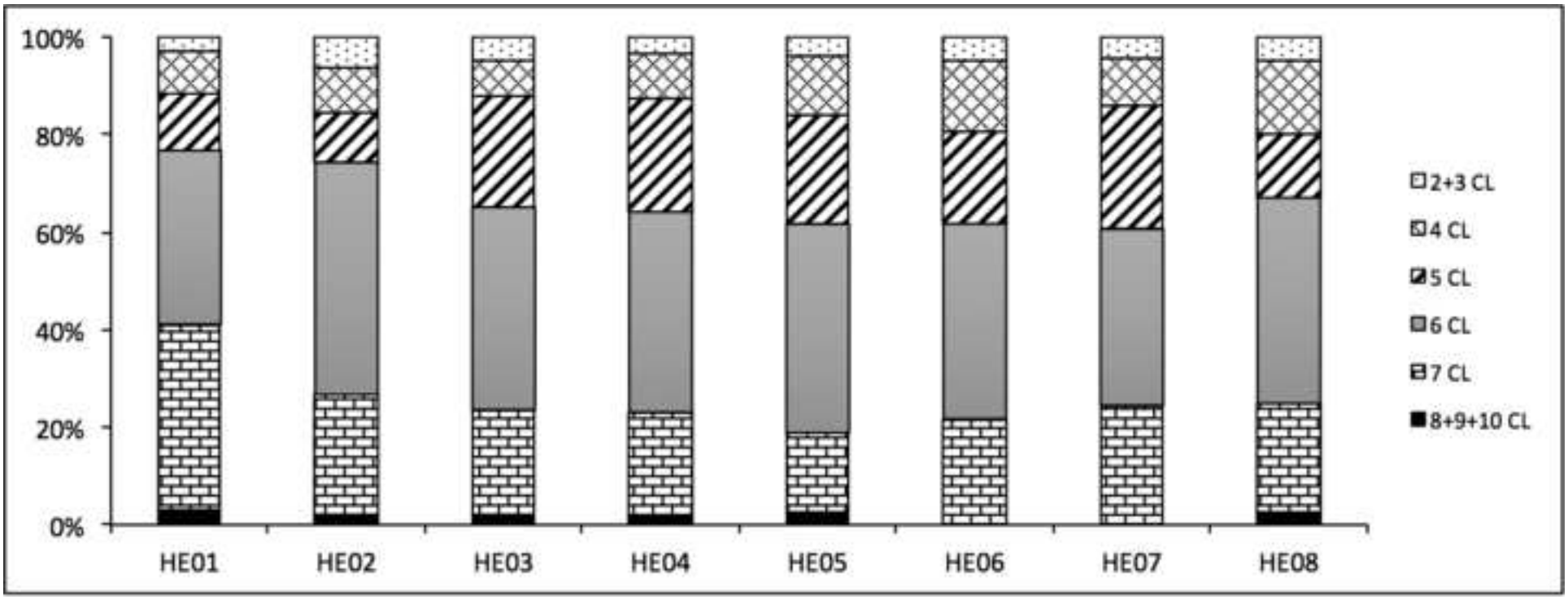
Figure(s) 3B

Click here to download high resolution image



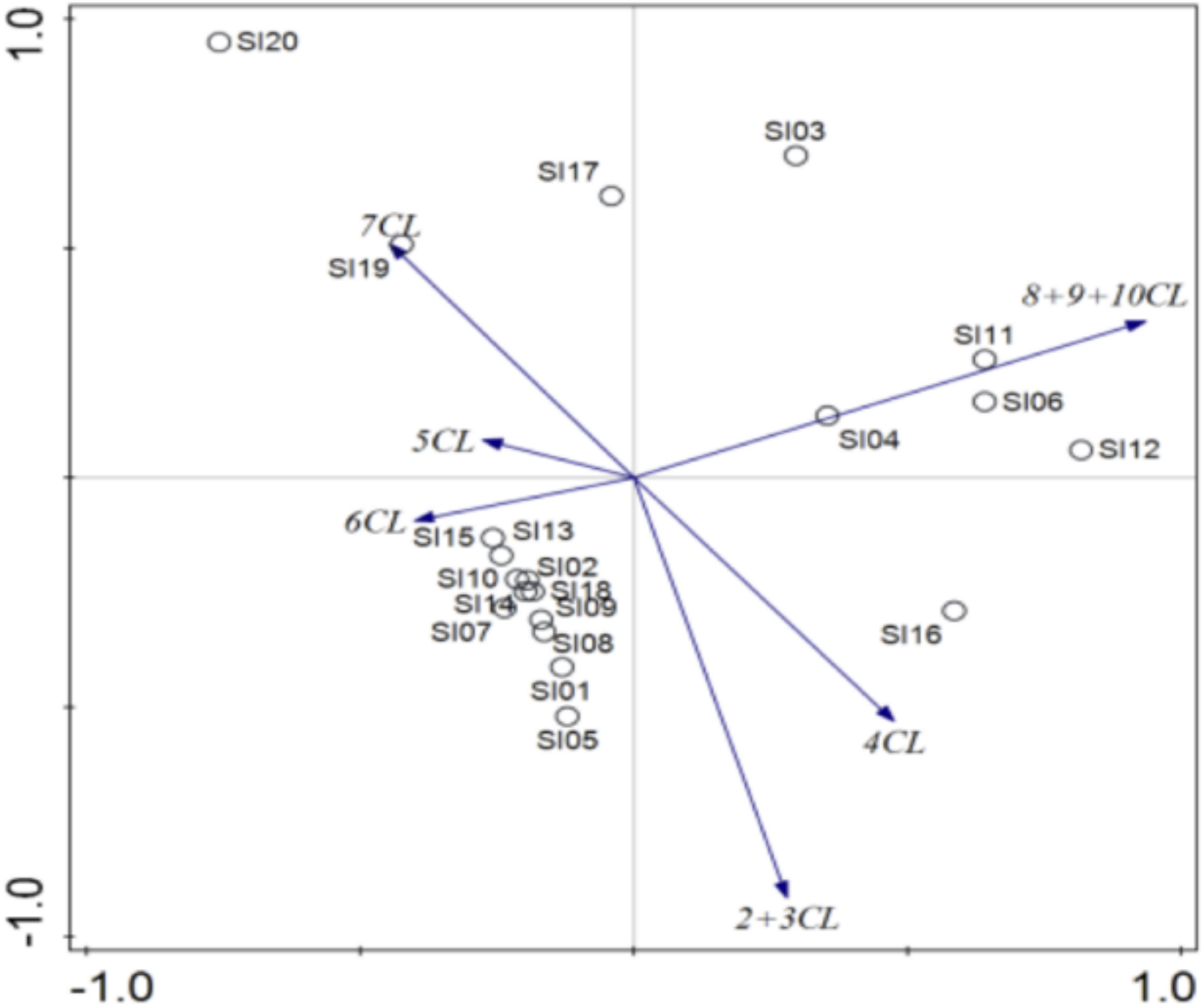
Figure(s) 3C

Click here to download high resolution image



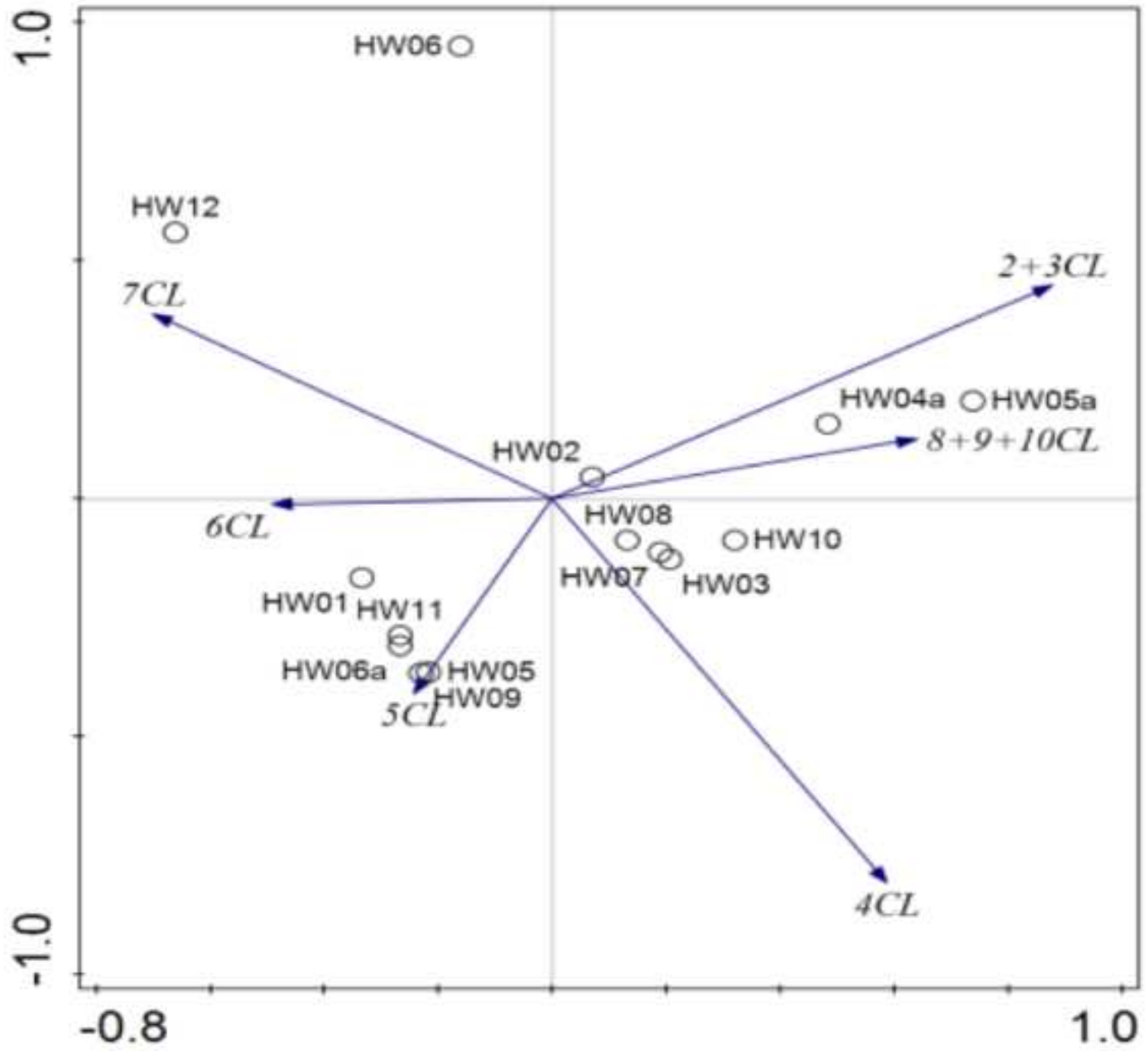
Figure(s) 4A

Click here to download high resolution image



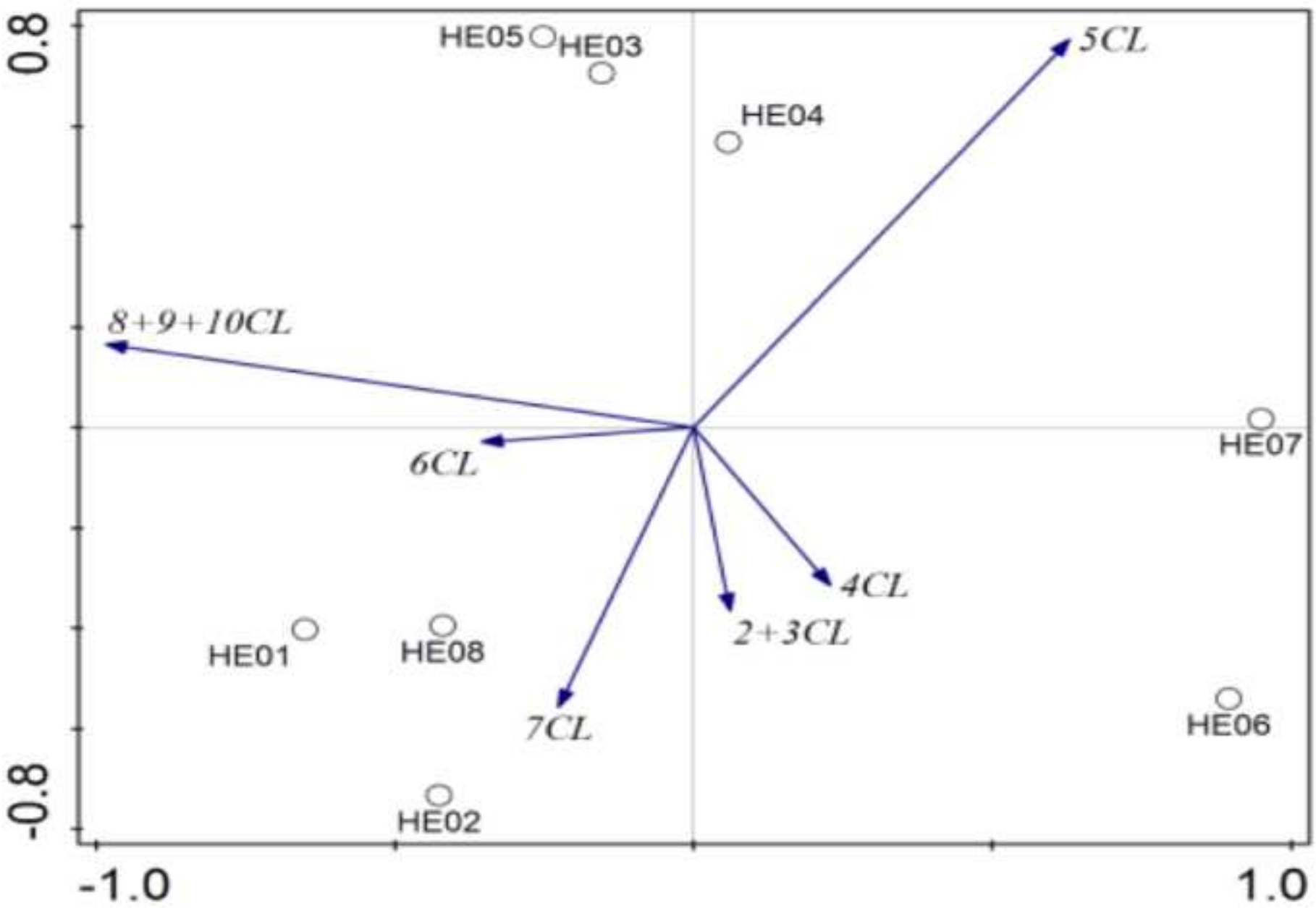
Figure(s) 4B

Click here to download high resolution image



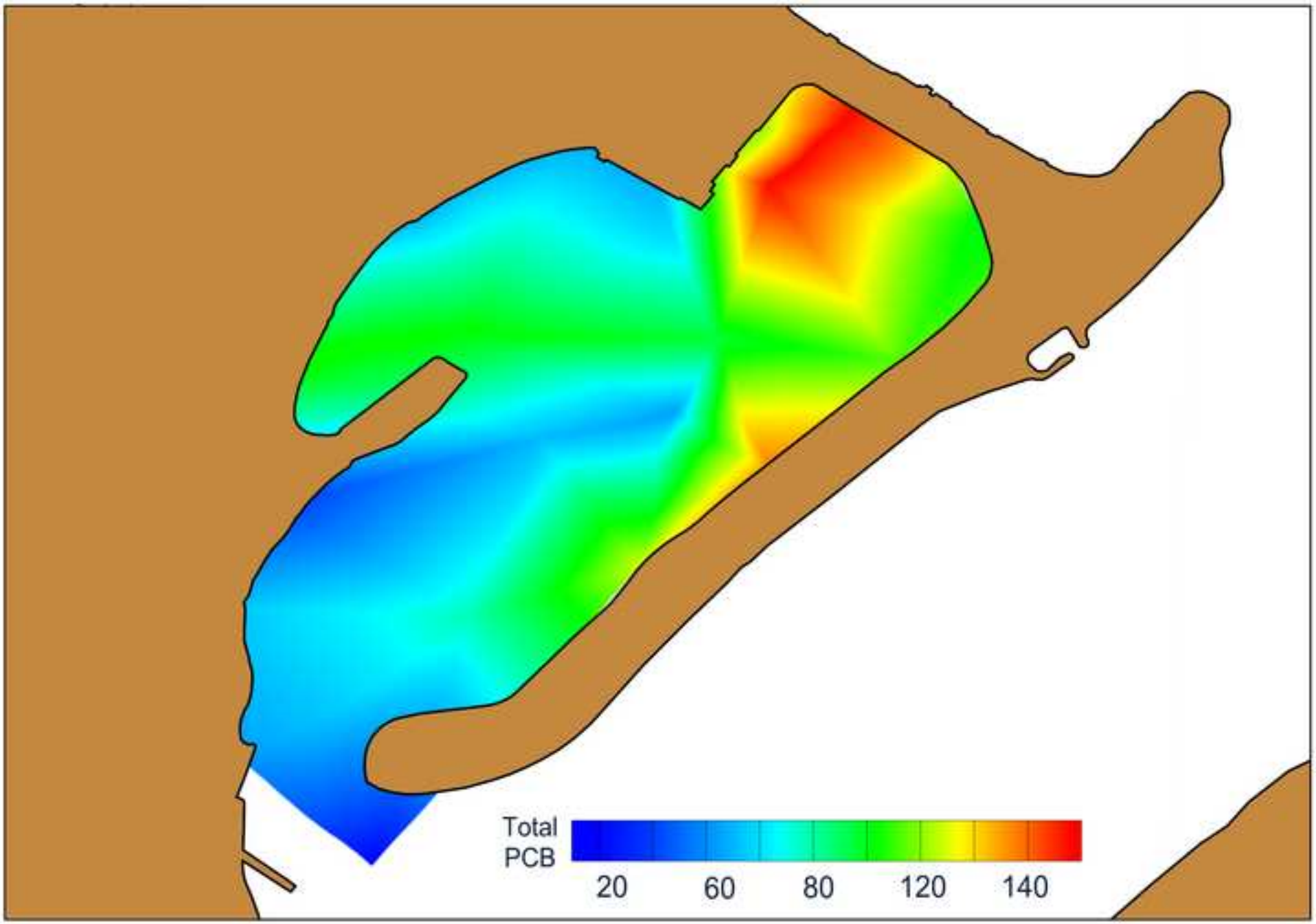
Figure(s) 4C

Click here to download high resolution image

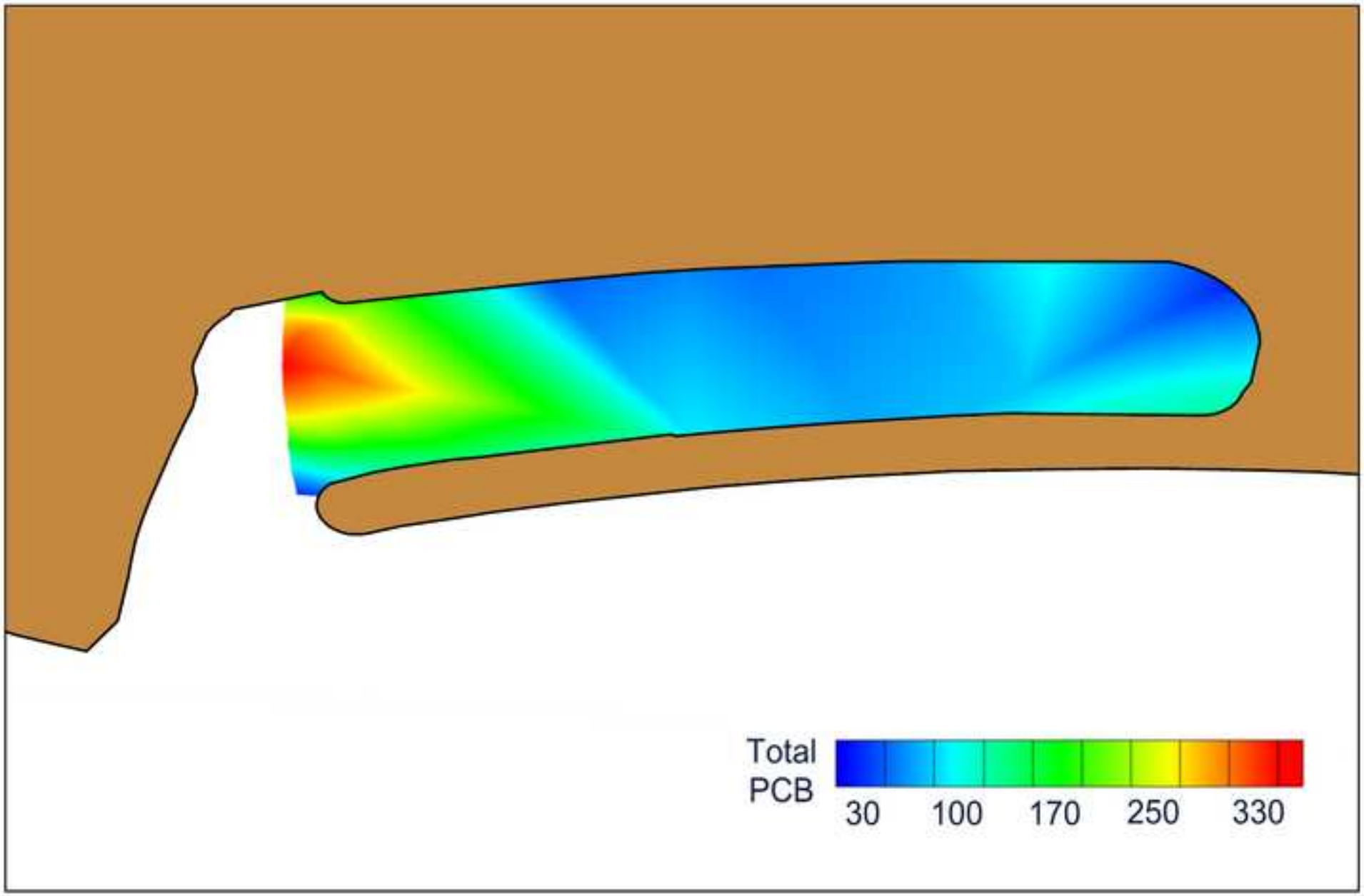


Figure(s) 5A

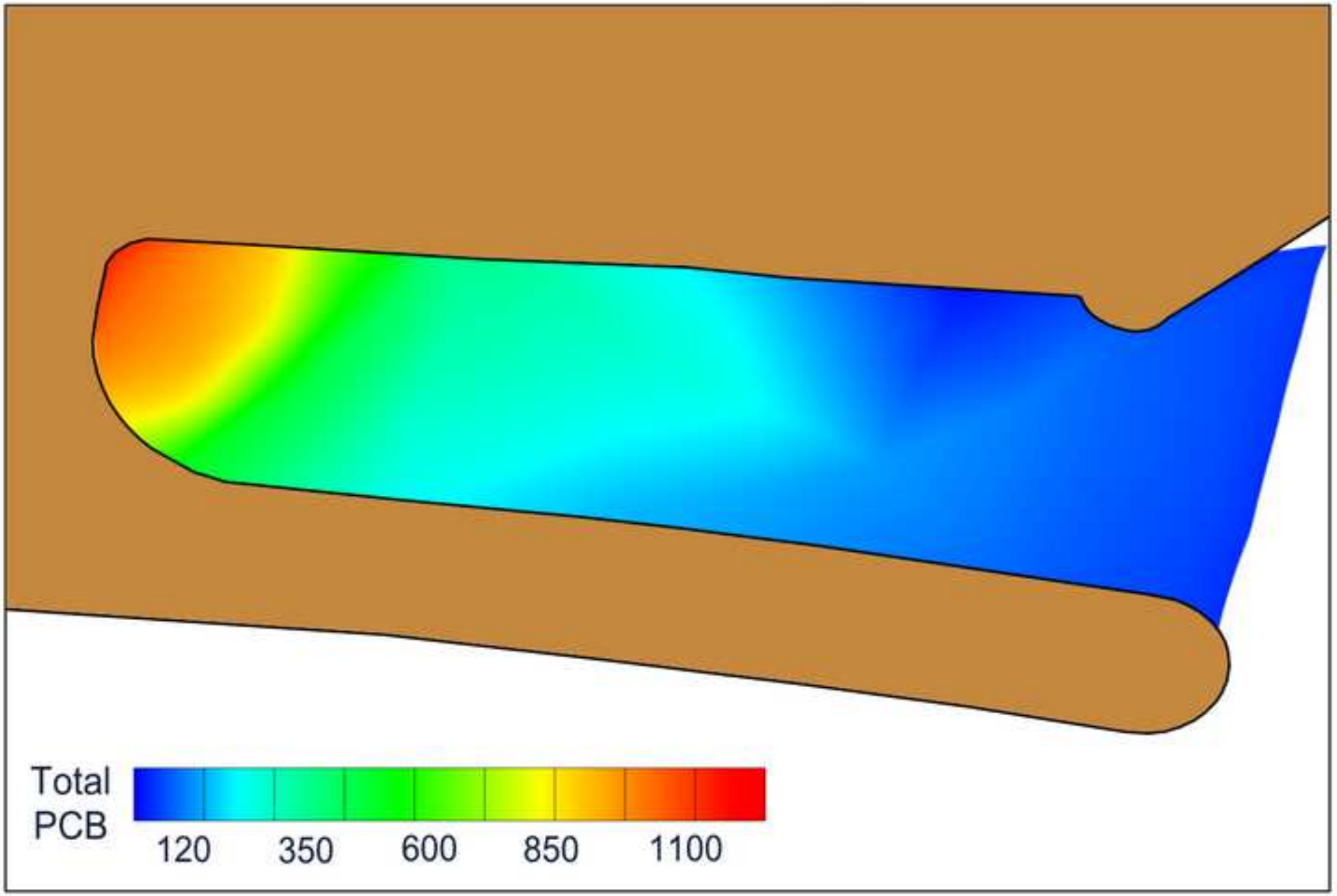
Click here to download high resolution image



Figure(s) 5B
Click here to download high resolution image



Figure(s) 5C
Click here to download high resolution image



Supplementary Data Table S1

Click here to download Supplementary Data: Suppl. Table S1_Neira_MPB-D-17-00964.docx

Supplementary Data Table S2

Click here to download Supplementary Data: Suppl. Table S2_Neira_MPB-D-17-00964.docx

Supplementary Data Table S3

Click here to download Supplementary Data: Suppl. Table S3_Neira_MPB-D-17-00964.docx

Supplementary Data Table S4

Click here to download Supplementary Data: Suppl. Table S4_Neira_MPB-D-17-00964.docx

Supplementary Data Table S5

Click here to download Supplementary Data: Suppl. Table S5_Neira_MPB-D-17-00964.docx

Supplementary Data Table S6

Click here to download Supplementary Data: Suppl. Table S6_Neira_MPB-D-17-00964.docx