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Polychlorinated biphenyl spatial patterns in San Francisco Bay forage fish

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HIGHLIGHTS

- ▶ Estuarine forage fish are useful biosentinels of site-specific PCB contamination.
- ▶ Contaminated industrial sites have elevated tissue PCB concentrations.
- ▶ A north–south spatial gradient was related to urbanization.
- ▶ Tissue concentrations correlated with co-located sediment concentrations.
- ▶ Congener profiles at some industrial sites indicated local Aroclor 1248 exposure.

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ABSTRACT

Industrialized waterways frequently contain nearshore hotspots of legacy polychlorinated biphenyl (PCB) contamination, with uncertain contribution to aquatic food web contamination. We evaluated the utility of estuarine forage fish as biosentinel indicators of local PCB contamination across multiple nearshore sites in San Francisco Bay. Topsmelt (*Atherinops affinis*) or Mississippi silverside (*Menidia audens*) contamination was compared between 12 targeted sites near historically polluted locations and 17 probabilistically chosen sites representative of ambient conditions. The average sum of 209 PCB congeners in fish from targeted stations (441 ± 432 ng g^{-1} wet weight, mean ± SD) was significantly higher than probabilistic stations (138 ± 94 ng g^{-1}). Concentrations in both species were comparable to those of high lipid sport fish in the Bay, strongly correlated with spatial patterns in sediment contamination, and above selected literature thresholds for potential hazard to fish and wildlife. The highest concentrations were from targeted Central Bay locations, including Hunter's Point Naval Shipyard (1347 ng g^{-1}; topsmelt) and Stege Marsh (1337 ng g^{-1}; silverside). Targeted sites exhibited increased abundance of lower chlorinated congeners, suggesting local source contributions, including Aroclor 1248. These findings indicate that current spatial patterns in PCB bioaccumulation correlate with historical sediment contamination due to industrial activity. They also demonstrate the utility of naturally occurring forage fish as biosentinels of localized PCB exposure.

1. Introduction

Polychlorinated biphenyls (PCBs) were produced and used in industrial applications from the 1930s until their ban in 1979. Elevated PCB concentrations in aquatic animals were first noted in the 1960s (Jensen et al., 1969), and remain a concern globally (e.g., Muir et al., 1999; Huang et al., 2006; Wu et al., 2008; Stahl et al., 2009). PCBs are environmentally persistent, bioaccumulative, and toxic compounds that pose health risks to humans and wildlife (Diamanti-Kandarakis et al., 2009). Sport fish contamination by total PCBs and PCBs with dioxin-like properties poses elevated risk of carcinogenic effects to humans in multiple US water bodies (Connor et al., 2005; Huang et al., 2006; Weis and Ashley, 2007; Stahl et al., 2009). As a result, management activities to reduce the impacts of PCBs include fish consumption advisories and attempts to reduce PCB mass and bioavailability in contaminated areas (Cho et al., 1999; US EPA, 2000; Gustavson et al., 2008).

Given the concern regarding human health impacts, many studies have quantified PCBs in sport fish used for human consumption (Rasmussen et al., 1990; Lamon and Stow, 1999; Davis et al., 2002; Fernandez et al., 2004; Greenfield et al., 2005; Huang et al., 2006; Parnell et al., 2008; Stahl et al., 2009). However, sport fish have limited utility for resolving contaminant spatial patterns within water bodies, because they often have large foraging ranges.

PCBs biomagnify in the aquatic food web and pose a range of toxic effects to aquatic mammals and birds at environmentally relevant concentrations, particularly via the Ah receptor mediated

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pathway (Giesy and Kannan, 1998; Van den Berg et al., 1998, 2006). As a result, PCB concentrations in piscivorous aquatic mammals (e.g., pinnipeds, cetaceans, mustelids), birds, and their prey are useful bioindicators of the hazard these compounds pose to aquatic ecosystems (van der Oost et al., 2003). Small fish consumed by piscivorous wildlife (i.e., forage fish) have been monitored for PCBs (Monosson et al., 2003; Pulster et al., 2005; Jarvis et al., 2008; Brar et al., 2010), albeit to a lesser extent than sport fish. Forage fish have been useful indicators of spatial patterns in mercury bioaccumulation within a water body (Suchanek et al., 2008; Greenfield and Jahn, 2010). Because forage fish are small and have limited home ranges, they may be particularly useful for discerning spatial patterns in food web exposure to PCBs and other industrial pollutants.

Concentrations of PCBs and toxicological impairment have been found to be highest in fish and invertebrates collected from industrial regions (Rasmussen et al., 1990; Myers et al., 1998; Johnson et al., 1999; Bayen et al., 2003; Wu et al., 2008; Brar et al., 2010), suggesting an association between historic production, use, and disposal of PCBs in adjacent industrial facilities, and biota exposure. Congener profile patterns have also been demonstrated to vary, with fish from contaminated locations often exhibiting elevated abundance of lower chlorinated congeners (Ashley et al., 2000; Barron et al., 2000; Fernandez et al., 2004), or higher chlorinated congeners (Pulster et al., 2005; Grant et al., 2011), depending on local production and use patterns.

In large river and coastal systems, broad spatial gradients of biota PCB concentrations have been observed, with concentrations declining with increasing distance from historic production facilities (Barron et al., 2000; Fernandez et al., 2004). However, few studies have examined spatial patterns within smaller water bodies, such as urbanized estuaries. These water bodies often have multiple potential sources, including numerous shoreline locations with a history of PCB use and contamination. Consequently, sediment PCB concentrations and congener profiles indicate local contamination of industrial areas, such as urbanized harbors (Ashley and Baker, 1999; Fu and Wu, 2006; Davis et al., 2007; Grant et al., 2011). The extent to which contamination at these nearshore sites enters the local aquatic food web is often unclear. If forage fish from industrially contaminated locations exhibit elevated concentrations, this would indicate food web exposure and validate the extensive remediation efforts underway (Cho et al., 1999; Gustavson et al., 2008).

We determined PCB congener concentrations in forage fish samples collected from 35 locations in San Francisco Bay (CA, USA), an urbanized estuary. We also compared PCB concentrations and dioxin TEQs to literature thresholds for potential effects to sensitive fish and piscivorous wildlife. Unlike previous studies, we employed a stratified probabilistic sampling design to fully characterize spatial variation in PCB contamination within a single urbanized estuary. Our study compared two strata: sites with elevated PCBs in sediments due to historic industrial activity, and randomly selected sites. The study addressed five questions: (1) what are the PCB concentrations and spatial patterns in San Francisco Bay forage fish? (2) do forage fish concentrations vary between random sites and industrial sites? (3) do concentrations pose a potential hazard to aquatic biota residing within San Francisco Bay? (4) how do forage fish PCB concentrations correlate with co-located sediment PCB concentrations? and (5) how do congener profile patterns vary among sites?

2. Methods

2.1. Study area

San Francisco Bay is an urbanized estuary with a land and water use history of industrialization. PCBs were employed in many applications and processes sited along the San Francisco Bay margins (Davis et al., 2007). Accordingly, parts of the Bay margins are contaminated (Hunt et al., 1998; Hwang et al., 2006), with several locations listed by the US Superfund cleanup program for PCBs and other pollutants (Battelle et al., 2005; Davis et al., 2007). Although sediment contamination and toxicity have been monitored in these locations, their contribution to local biota contaminant exposure has not been systematically evaluated.

2.2. Site selection

In 2007, six stations were sampled as part of a pilot study: Alviso Slough, Newark Slough, Steinberger Slough, Candlestick Point, Point Isabel, and Benicia State Park. These stations were chosen to represent the different Bay sub-embayments, focusing on important sites for piscivorous wildlife and habitat management (Greenfield and Jahn, 2010). In 2010, 29 sites were sampled from two strata: (1) a probabilistic survey to reflect ambient conditions, and (2) sites targeted due to historical contamination in sediment. The probabilistic sites, representing ambient conditions throughout the Bay shoreline, were obtained using a Generalized Random Tessellation Stratified (GRTS) design (Stevens and Olsen, 2004). Probabilistic sites were drawn from two substrata: the open bay shoreline (nine sites), and sub-embayments (including marinas and estuarine backwater channels; seven sites). The targeted sites were chosen to represent conditions of potentially elevated PCB exposure to forage fish, based on previously collected data on sediment contamination (see Supplemental information for data sources). Targeted sites included all monitored nearshore locations that either contained Bay sediment PCB concentrations > 100 ng g^{-1} dry weight, or received discharge from storm drains or conveyances containing sediment PCB concentrations > 1000 ng g^{-1} (SFEI, 2010).

2.3. Field sampling

All sampling was performed in 2007 and 2010, using a beach seine towed in nearshore locations. Target species were Mississippi silverside (*Menidia audens*) and topsmelt (*Atherinops affinis*); both species are small (40–100 mm) forage fish that have restricted home ranges, nearshore habits, wide distribution, and similar diets (Greenfield and Jahn, 2010). Topsmelt are abundant in Lower South Bay, South Bay and Central Bay. Silversides inhabit lower salinities than topsmelt, and are abundant in sub-embayments of Lower South Bay, San Pablo Bay, and Suisun Bay, as well as sites where freshwater drainages meet the Bay.

Separate composite samples of topsmelt were collected from six sites between September 24 and October 9, 2007. Between September 22 and November 10 of 2010, Alviso Slough was resampled, and 28 new sites were sampled, including 15 probabilistic sites, and 13 targeted sites, with a total of 31 composite samples collected at 29 different sites. Based on species occurrence, silverside were collected and analyzed at 14 sites, and topsmelt at 17 sites. Both species were sampled at Alviso Slough as well as at the targeted site in San Rafael channel (Table 1).

Samples were analyzed as homogenized whole body composites, with target fish total lengths of 60–100 mm for topsmelt and 40–80 mm for silverside. Topsmelt samples ranged from 8 to 16 individuals per composite (mean = 11), with mean fish length of 90 ± 5 mm (mean ± SD) in 2007 and 77 ± 8 mm in 2010. Silverside samples ranged from 13 to 38 individuals per composite (mean = 23), with average fish length of 61 ± 5 mm.

2.4. Laboratory analysis and quality assurance

In 2007, samples were analyzed for 40 separately resolved PCB congeners. Samples collected in 2010 were analyzed for all 209

Table 1
Sample information and PCB and dioxin TEQ concentrations (wet weight) for study samples.

Site name	Site ID	Species[a]	Year	Targeted[b]	Sum 40 congeners (ng g^{-1})	Sum 209 congeners (ng g^{-1})	Mammalian dioxin TEQ (pg g^{-1})	Avian dioxin TEQ (pg g^{-1})	Lipid (%)
Alviso Slough	ALVSL	Top	2007		137.3				4.43
Benicia Park	BENPK	Top	2007		136.9				3.64
Bird Island	BIRDI	Top	2007		169.2				4.08
Candlestick Park	CANDL	Top	2007		421.8				3.08
Newark Slough	NEWSL	Top	2007		115.9				3.63
Point Isabel Outer	PTISO	Top	2007		142.5				3.39
Average 2007					*187.3*				*3.71*
Alviso Slough	ALVIS-M	Mis	2010	N	82.6	98.7	1.36	2.63	4.31
Alviso Slough	ALVIS-T	Top	2010	N	128.5	154.6	1.73	4.10	3.97
Central Bay, North of SF Airport	23OTH	Top	2010	N	279.3	332.9	5.49	10.3	3.93
Coyote Creek East	28OTH	Mis	2010	N	220.7	266.6	3.61	6.56	3.89
Eden Landing Shoreline	81OTH	Top	2010	N	101.8	122.7	2.17	4.66	3.99
Emeryville	80OTH	Top	2010	N	217.7	261.5	5.34	11.7	3.43
Lower South Bay, Near Stevens Creek	77OTH	Mis	2010	N	152.7	183.2	2.82	4.73	3.60
Mission Creek	78OTH	Top	2010	N	134.5	162.3	2.37	3.53	2.02
Napa River	26OTH	Mis	2010	N	28.7	34.1	0.51	0.91	2.34
Newark Slough	24OTH	Top	2010	N	107.0	129.3	1.58	3.70	4.00
North San Pablo Bay, Western Shore	90OTH	Mis	2010	N	44.3	52.9	0.96	1.42	1.87
Petaluma Marsh	22OTH	Mis	2010	N	38.5	45.3	0.76	1.26	2.24
Redwood City Boat Ramp	20OTH	Top	2010	N	216.2	260.6	4.01	8.10	4.06
South Bay, Near Coyote Point	85OTH	Top	2010	N	140.3	169.8	2.65	5.10	3.90
South San Pablo Bay near Hercules	SPBAY	Top	2010	N	63.9	76.6	0.89	1.79	3.46
Suisun Bay, at Port Chicago	79OTH	Mis	2010	N	47.6	56.9	0.12	0.57	1.90
Suisun Bay East, at Winter Island	83OTH	Mis	2010	N	31.7	38.0	0.67	0.98	2.16
Suisun Marsh Near Cutoff Slough	25OTH	Mis	2010	N	25.2	30.5	0.48	0.70	1.51
Average 2010 Probabilistic					*114.5*	*137.6*	*2.08*	*4.04*	*3.14*
Alameda Seaplane Harbor	SEAPL	Top	2010	Y	162.4	203.8	4.41	8.22	2.98
Hunter's Point North	HUPTN	Top	2010	Y	189.7	228.3	3.10	4.82	2.75
Hunter's Point South Basin	SOBAS	Top	2010	Y	1132	1347	14.3	22.8	4.20
Mare Island	MARIS	Mis	2010	Y	43.8	52.5	1.61	2.17	2.89
North San Leandro Bay	NSLB	Mis	2010	Y	303.1	358.8	1.77	4.86	1.87
Oakland Inner Harbor	OAKIH	Top	2010	Y	589.2	699.9	11.6	19.5	3.97
Oakland Middle Harbor	OMHEA	Top	2010	Y	142.0	169.4	3.71	6.62	3.66
Point Potrero	PPOT2	Top	2010	Y	187.4	224.9	3.67	7.16	3.88
Richmond Inner Harbor	11OTH	Top	2010	Y	342.1	415.3	6.97	13.1	3.84
San Leandro Harbor, at Davis Creek	SANLE	Mis	2010	Y	329.5	398.6	6.78	9.37	1.98
San Rafael Creek	SANRA-M	Mis	2010	Y	126.3	148.2	3.36	4.62	1.82
San Rafael Creek	SANRA-T	Top	2010	Y	125.6	150.0	2.60	4.74	3.38
Stege Marsh	STEGE	Mis	2010	Y	969.9	1337	8.27	29.4	2.40
Average 2010 Targeted					*357.1*	*441.0*	*5.55*	*10.6*	*3.05*

[b] N = probabilistic site for ambient conditions; Y = targeted (industrial) site.
[a] Top = topsmelt; Mis = Mississippi silverside.

congeners (Σ209 congeners). This included the 40 PCB congeners (Σ40 congeners) routinely analyzed in tissue samples by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP): PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203. In 2007, 36 of the Σ40 congeners were determined (excluding PCBs 44, 128, 132, and 151).

Samples were spiked with ^{13}C labeled surrogate standards, dried with sodium sulfate, Soxhlet extracted with dichloromethane, and analyzed for PCBs using US EPA Method 1668A. All analyses were performed by isotope dilution high resolution gas chromatography/high resolution mass spectrometry, by AXYS Analytical Services (Sidney, BC, Canada). In Method 1668A, 126 congeners are resolved as separate chromatographic peaks and the remaining 83 PCB congeners coelute in groups of two to six congeners (US EPA, 2003). Lipid content was determined by gravimetric analysis, with dichloromethane as the extraction solvent (US EPA, 2000). QA samples included three procedural blanks, three laboratory spiked reference material samples, three Certified Reference Material (CRM, NIST 1946) samples, three duplicates, and two matrix spikes. The Supplemental information contains a QA results summary.

2.5. Comparison to literature effects thresholds

Forage fish tissue PCB concentrations and dioxin TEQs were compared to effects thresholds for fish and piscivorous aquatic wildlife. Aquatic piscivore effects thresholds included a No Observed Adverse Effect Concentration (NOAEC) based on total PCBs (72 ng g^{-1} ww) and dioxin TEQs (0.3 pg g^{-1} ww) in mink (*Mustela vison*) diets (Giesy and Kannan, 1998); a set of geometric mean values at which dietary concentrations exhibited toxic effects to aquatic mammals for total PCBs (89 ng g^{-1} ww) and dioxin TEQs

(1.6 pg g^{-1} ww, Kannan et al., 2000); and the mammalian (0.77 pg g^{-1} ww) and avian (2.4 pg g^{-1} ww) predator dioxin TEQs screening values developed by Environment Canada (Environment Canada, 1998). For hazard to fish, lipid weight concentrations were compared to a total PCB threshold (2400 ng g^{-1} lipid) developed to protect salmonids from sublethal effects (Meador et al., 2002). Hazard quotients (HQ = average concentration/threshold) and proportion of samples exceeding each threshold were calculated. Because salmonids and mink are relatively sensitive taxa to dioxin-like toxicity of PCBs (Elonen et al., 1998; Kannan et al., 2000), the threshold comparisons are conservative screening assessments of hazard, and are not site specific. HQ < 1 indicate an absence of risk of effects, whereas HQ $\geqslant$ 1 indicates uncertainty regarding effects. Separate calculations were performed for each site category (2007 sites, 2010 probabilistic, and 2010 targeted).

2.6. Comparison to sediment PCBs

To determine association with legacy sediment contamination, fish Σ40 PCB congener concentrations were regressed against total PCBs in sediments, using previously published data (Barnett et al., 2008; SFEI, 2010). The Supplemental information provides further details on the sediment data used in the regressions. Given that fish and sediment data were not co-located, the average sediment concentration was determined within a 4 km radius of each fish collection location, and the results were regressed against fish tissue concentrations (Melwani et al., 2009). There were 35 fish collection events having between 1 and 71 sediment samples within a 4 km radius (average 19 sediment samples per fish sample). To determine the extent of bioaccumulation, and enable comparison to previous studies, the biota sediment accumulation factor (BSAF) was also calculated as BSAF = [tissue PCBs (ng g^{-1} lipid)/sediment PCBs (ng g^{-1} organic carbon)] (Ankley et al., 1992; van der Oost et al., 2003).

2.7. Data analysis

All statistical analyses were performed in R version 2.15 (R Development Core Team, 2012). Σ40 and Σ209 PCB congeners and dioxin-like potency were determined for each sample using Kaplan–Meier estimation for summary statistics in the presence of censored data (Helsel, 2010). Dioxin-like potency was calculated for the planar PCBs (77, 81, 105, 114, 118, 126, 156, 157, 167, 169, and 189) for samples collected in 2010 only. PCB 123 was excluded due to poor recovery of certified reference material (Supplemental information). Dioxin-like potency was calculated as dioxin toxic equivalents (TEQs), using the WHO 1998 toxic equivalency factors (TEFs) for birds and fish and the WHO 2005 revised TEFs for mammals (Van den Berg et al., 1998, 2006).

For all statistical analyses, PCBs were natural log transformed to achieve normality and variance homoscedasticity of the residuals. Analyses were performed using the linear model (lm) procedure in *R*. Linear models were performed on 2010 wet weight data to evaluate the effect of four predictor variables on Σ209 PCB congeners (response variable). Predictor variables included site type (targeted versus random), species (topsmelt versus silverside), tissue lipid (%), and distance from the Guadalupe River (river km). Candidate models included all possible linear combinations of these predictors, in addition to three interaction terms with plausible underlying mechanisms: site type versus species, site type versus distance from Guadalupe River, and species versus distance from Guadalupe River (Supplemental Table S1). A separate linear model analysis was also performed on lipid weight data, including all variables except tissue lipid (Supplemental Table S2).

Distance from Guadalupe River is the aquatic surface distance (in river km) from a primary tributary located at the southern extent of the Lower South Bay. The Lower South Bay has elevated concentrations of many contaminants due to high watershed development and lower Bay flushing rate (Conaway et al., 2003; Oros et al., 2005; Davis et al., 2007). Distance from the Guadalupe River primarily serves as a quantitative proxy for broad spatial variation in the Bay, more accurate than latitude because it accounts for the half-moon shape of the Bay.

The candidate models were compared using an information theoretic approach, in which the relative goodness of fit was contrasted, and models that simply and effectively explained variability in Σ209 PCBs (response variable) were selected (Burnham and Anderson, 2002). Model evaluation was performed based upon the AICc (Akaike information criterion with bias adjustment for small sample sizes), a metric for comparing the relative fit among a set of candidate models (Burnham and Anderson, 2002). The model with the minimum AICc is considered the best model, based on a combination of fit to the observed data and model parsimony (i.e., minimum number of model parameters). Model comparison was aided with the ΔAICc ($\Delta AICc_i = AICc_i -$ minimum AICc of all models), with models having ΔAICc < 2.0 being considered comparable; and the Akaike weight ($w_i = \exp[-\Delta AICc_i/2]/\Sigma \exp[-\Delta AICc_i/2]$), used to determine the degree of confidence that the selected model was the best model. Importance of each predictor variable, relative to the other three predictor variables (i.e., variable weight), was determined by summing Akaike weights across models that incorporated the same variable (Burnham and Anderson, 2002). For all linear models, adjusted R^2 was reported to indicate the extent of variability explained.

Principal component analysis (PCA) was performed on the concentrations of individual congeners from the 2010 samples to help evaluate variation in congener patterns across sites. For each site, the congener concentrations were normalized to the Σ209 PCBs to eliminate the effect of total concentration on the first principal component. The statistical analysis was performed on the log-transformed relative abundances of each congener. The PCA was performed on 131 unique congener values. The Supplemental information describes congener inclusion criteria in the PCA.

3. Results

In 2007, six topsmelt samples were analyzed from six stations. In 2010, 14 silverside and 17 topsmelt samples were analyzed from 29 stations (Table 1). Lipid content of silversides (2.5 ± 0.9%, mean ± SD) was lower than topsmelt in 2007 (3.7 ± 0.5) and 2010 (3.6 ± 0.6). Lipid weight congener concentrations were strongly correlated with wet weight concentrations (linear regression on log-transformed Σ40 congener data $p < 0.0001$; $R^2 = 0.89$). All tissue results are reported in wet weights (ww), except where indicated otherwise.

Topsmelt from 2007 exhibited an average Σ40 PCB congeners of 187 ± 116 ng g^{-1}. All individual station measurements were within 95% CI of the mean except for Candlestick Park (422 ng g^{-1}). Concentrations in the 31 fish samples analyzed in 2010 averaged 216 ± 253 ng g^{-1} for Σ40 PCB congeners, 265 ± 321 for Σ209 PCB congeners, and 3.5 ± 3.2 pg g^{-1} dioxin TEQ for the 12 congeners with dioxin-like potency. All field and analytical results are provided in Supplemental data files SDat1PCBs.csv and SDat2Samples.csv.

Concentrations (Σ209 PCB congeners) in 2010 were lognormally distributed, with 24 of 31 samples below 200 ng g^{-1}, and two samples above 1300 ng g^{-1} (Table 1). The four highest concentrations were all from targeted stations: South Basin of Hunters Point (topsmelt, 1347 ng g^{-1}), Stege Marsh (silverside, 1337 ng g^{-1}), Oakland Inner Harbor (topsmelt, 700 ng g^{-1}), and Richmond Inner Harbor (topsmelt, 415 ng g^{-1}). The seven lowest concentrations, ranging between 31 and 57 ng g^{-1}, were all San

Pablo Bay and Suisun Bay silverside (Table 1, Fig. 1). PCBs ranged 44-fold between the lowest (31 ng g^{-1}) and highest (1347 ng g^{-1}) sites.

The relationship between Σ40 congeners and Σ209 congeners was examined using a regression between the Σ40 congeners and the sum of the remaining 169 congeners. A natural log transformation was applied to both Σ40 and Σ169 congeners to achieve normally distributed residuals with variance homoscedasticity. Regression analysis indicated a highly significant log–log relationship ($p < 0.0001$; $R^2 = 0.98$; Supplemental Fig. S1); however, the Stege Marsh silverside sample was an influential positive outlier and was consequently removed to obtain an unbiased fit ($R^2 = 0.99$). The final model to predict Σ209 congeners from Σ40 congeners is:

$$\Sigma 209 \quad \text{congeners} = (\Sigma 40 \quad \text{congeners}) - 1.643 + \exp[-1.6431 + 1.0064 * \ln(\Sigma 40 \text{ congeners})]$$

Between half and all of samples from each stratum exceeded all effects thresholds (Table 2). In particular, all six samples collected in 2007 exceeded both PCB concentration thresholds, and between 11 and 13 of 13 targeted samples from 2010 exceeded all PCB and dioxin TEQ effects thresholds. For all site types and thresholds, HQs were greater than one (Table 2). These results indicate that PCB concentrations in San Francisco Bay topsmelt and silverside are generally above concentrations at which there is no hazard of effects to fish or piscivorous wildlife.

3.1. Predictors of fish PCBs

In 2010, the historically contaminated targeted locations had elevated fish PCB concentrations, compared to the probabilistic ambient locations, for wet weight concentrations (Fig. 2) and lipid weight concentrations (Supplemental Fig. S2). Average Σ209 PCB congeners in fish from targeted stations (441 ± 432 ng g^{-1} wet weight) was 3.2 times concentrations from probabilistic stations (138 ± 94 ng g^{-1}). Average concentrations in topsmelt (301 ± 306 ng g^{-1}) were higher than silverside (222 ± 344 ng g^{-1}) for all stations, and particularly for probabilistic stations (185 ± 82 versus 90 ± 82 ng g^{-1}; Fig. 2). For all samples, wet weight concentrations

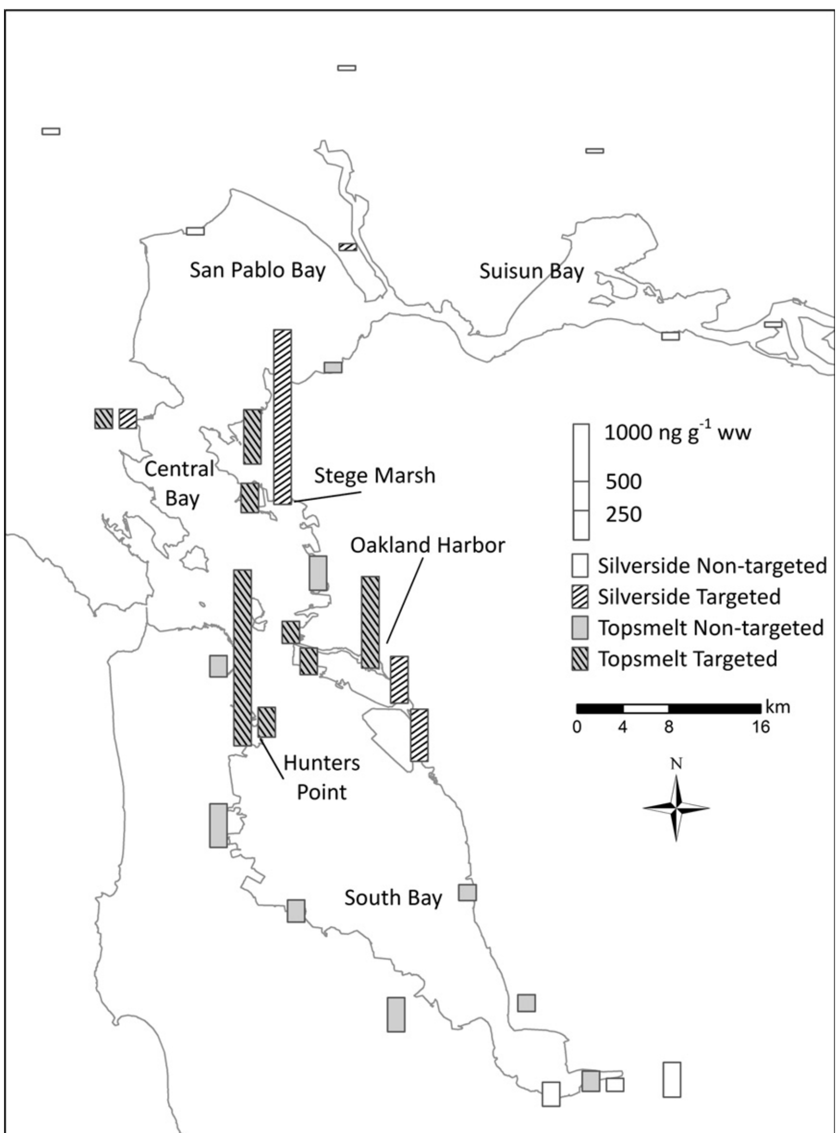

Fig. 1. Sum of 209 PCB wet weight concentrations at each location.

Table 2
Comparison of sample tissue concentrations to selected hazard thresholds for fish PCBs and dioxin TEQs. $N \geqslant$ indicates number of samples in stratum that exceed threshold. HQ indicates hazard quotient (average sample concentration/threshold concentration). (+) indicates HQ $\geqslant$ 1.

Threshold	Description	Reference	2007 (N = 6)[a]		2010 Probabilistic (N = 18)[b]		2010 Targeted (N = 13)[b]	
			$N\geqslant$	HQ	$N\geqslant$	HQ	$N\geqslant$	HQ
72 ng g^{-1} ww	Mink NOAEC	Giesy and Kannan (1998)	6	2.6 (+)	11	1.9 (+)	11	6.1 (+)
2400 ng g^{-1} lipid	Juvenile salmonid sublethal effects	Meador et al. (2002)	6	2.2 (+)	12	1.7 (+)	12	6.3 (+)
0.3 pg g^{-1} TEQ	Mink NOAEC	Giesy and Kannan (1998)			17	6.9 (+)	13	19 (+)
0.77 pg g^{-1} TEQ	Mammalian tissue residue guideline	Environment Canada (1998)			13	2.7 (+)	13	7.2 (+)
2.4 pg g^{-1} TEQ	Avian tissue residue guideline	Environment Canada (1998)			11	1.7 (+)	12	4.4 (+)
1.6 pg g^{-1} TEQ	Aquatic mammal effects threshold	Kannan et al. (2000)			9	1.3 (+)	13	3.5 (+)

[a] Based on Σ40 PCB congeners.
[b] Based on Σ209 PCB congeners and mammalian and avian dioxin TEQs.

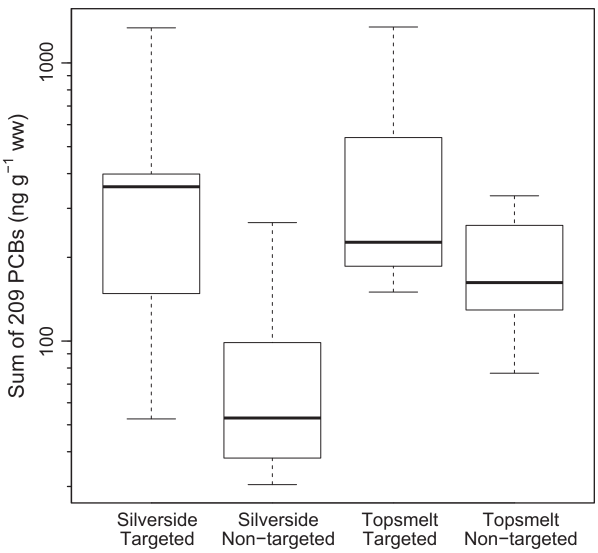

Fig. 2. Box and whisker plot of PCB wet weight concentrations across species and site type (targeted versus non-targeted). Thick line represents median concentration, box represents 25th and 75th percentile, and whiskers represent 95% confidence intervals. *Note*: log scale.

decreased with distance from the Guadalupe River (Pearson's $r = -0.47$) and increased slightly with increased lipid ($r = 0.36$).

Model comparisons provided strong evidence that site type and distance from the Guadalupe River influenced fish PCB concentrations. Based on AICc, ΔAICc, and Akaike weight, the most parsimonious model explaining fish PCBs (wet weight) in 2010 included site type (targeted versus random), distance from the Guadalupe River, and an interaction term for site type versus distance from the Guadalupe River (Supplemental information Table S1). The same model without an interaction term was also highly likely (ΔAICc = 0.2), and a model including species, site type, and distance from the Guadalupe River, was also reasonably likely (ΔAICc = 1.0). The next most likely model (ΔAICc = 2.1) included site type, species, and lipid. Using evidence ratios (i.e., quotient of the Akaike weights), the best model with site type, distance from Guadalupe River, and the interaction term was only 1.1 times more likely than the model that lacked the interaction term, and 2.9 times more likely than the third best model, including site type, lipid, and distance from the Guadalupe River. Based on variable weight (the sum of all Akaike weights for each model term), there was strong support for site type (variable weight = 1.00) and distance from Guadalupe River (variable weight = 0.99), and weak support for species (0.25) and lipid (0.17). Model comparison results were essentially the same for lipid weight data, with the most parsimonious model including site type, distance from the Guadalupe River, and an interaction term between these terms (Supplemental Table S2), and variable weights greater than 0.96 for site type and distance from the Guadalupe River.

Overall, concentrations were higher at the sites located towards the Central Bay and South Bay. Concentrations were relatively low in samples collected from San Pablo Bay and Suisun Bay, including the Mare Island targeted site collected northeast of San Pablo Bay (Fig. 1). The concentration decline with distance from the Guadalupe River was more apparent for probabilistic sites than targeted sites, resulting in the most parsimonious model including an interaction between site type and distance from the river. In particular, Stege Marsh, one of the most contaminated sites, was one of the farthest targeted sites from the Guadalupe River.

Fish and sediment PCB concentrations were positively related (Fig. 3). Using wet weight Σ40 congener tissue data versus dry weight sediment data (all log transformed), the relationship had an R^2 of 0.52 (N = 35), and a ΔAICc of −32.5 compared to the null (i.e., intercept only) model. The relationship was slightly weaker using lipid weight tissue data versus organic carbon corrected (i.e., ng g^{-1} organic carbon) sediment data, with an R^2 of 0.42 (N = 35), and a ΔAICc of −23.8 compared to the null model. The linear model to predict fish wet weight Σ40 congener concentrations from sediment dry weight concentrations was: fish PCBs = exp[3.386 + 0.589 * ln(Sediment PCBs)]. Examining species individually, the relationship was stronger for topsmelt (R^2 = 0.62, ΔAICc versus null = −19.9, N = 23) than silverside (R^2 = 0.39, ΔAICc = −9.1, N = 12) (Fig. 3). For silverside, the median BSAF (ng g^{-1} lipid/ng g^{-1} organic carbon) was 4.2 and the range was 1.7–31.7

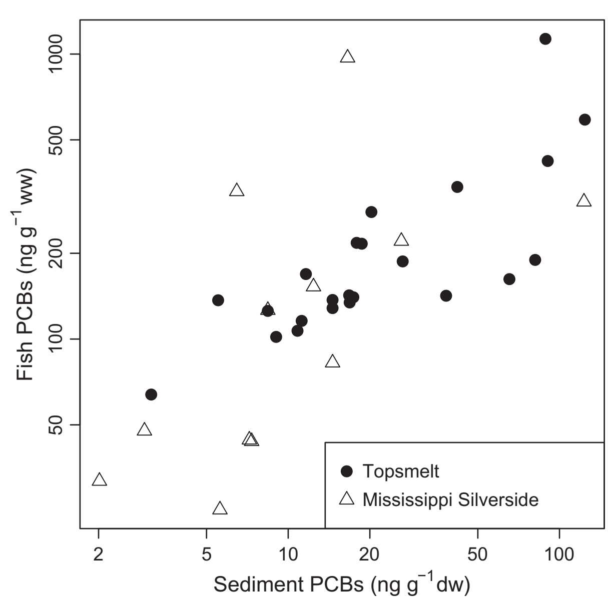

Fig. 3. Relationship between sediment and fish PCB concentrations (Σ40 congeners). *Note*: log scale.

($N = 12$). For topsmelt, the median BSAF was 3.2 and the range was 1.1–6.7 ($N = 23$).

3.2. PCB congener patterns

In a principal component analysis (PCA) of the 2010 individual PCB congener data, the first two principal components accounted for 64% and 9% of the variation between sites, respectively. Examining the relative contributions of each congener to the principal component axes (the eigenvectors, Supplemental Fig. S3), the heavier congeners generally contributed positively to the first principal component (PC1) axis, while the lighter congeners contributed negatively (Supplemental Fig. S3a). PC1 was significantly correlated with the ratio of the sum of the light congeners

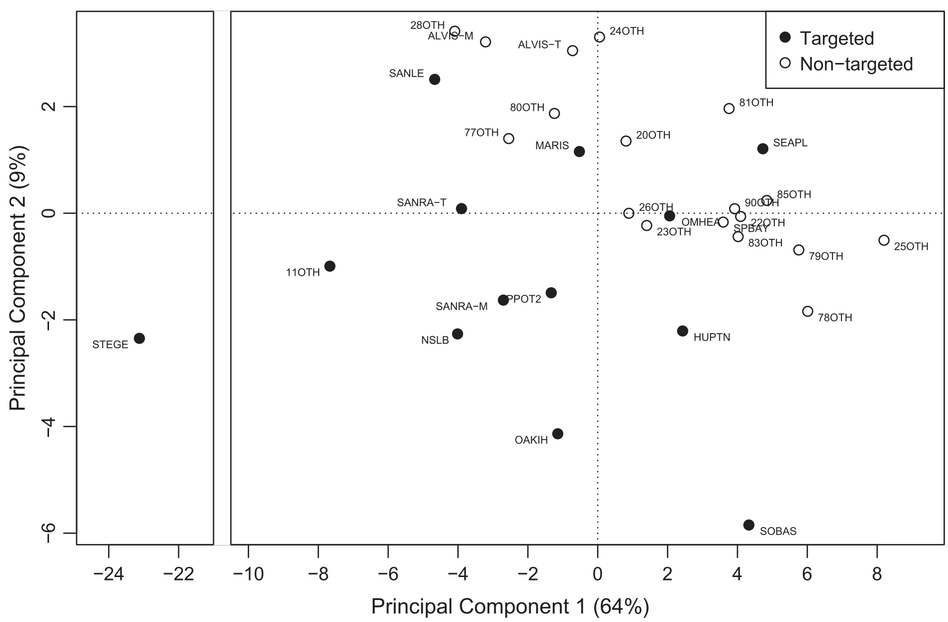

Fig. 4. Biplot of sites as separated out by the first two principal components. Abbreviations follow Table 1.

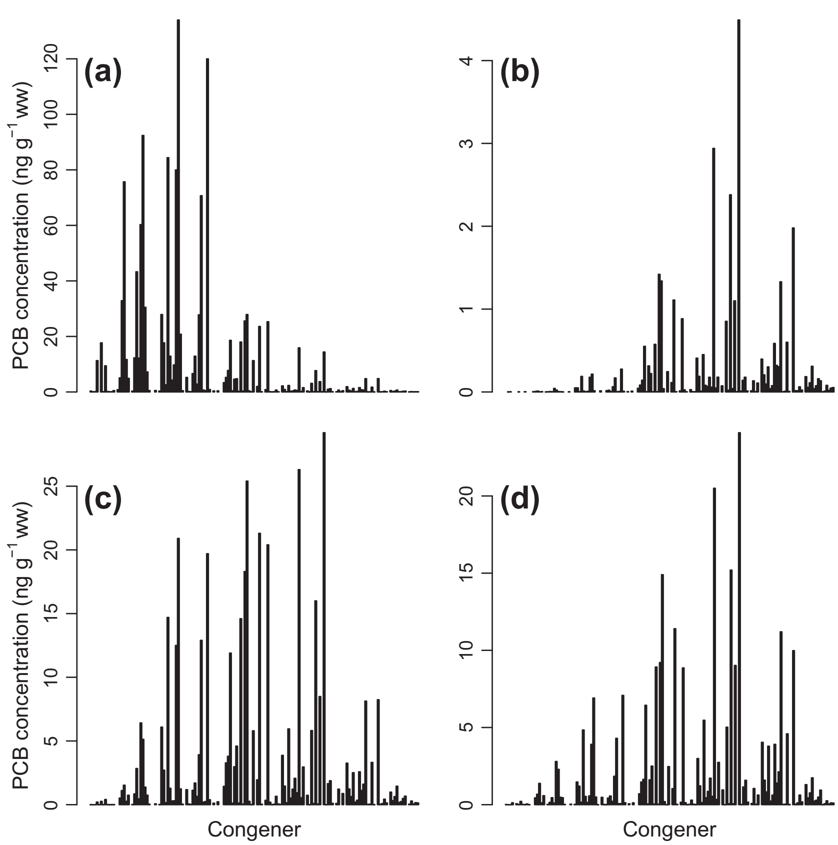

Fig. 5. Congener profiles for (a) Stege Marsh (STEGE), (b) Suisun Marsh (25OTH), (c) Richmond Inner Harbor (11OTH), and (d) Coyote Creek East (28OTH).

(mono- to tetra-substituted) to the sum of the heavy congeners (penta- to deca-substituted) ($p < 0.001$, adjusted $R^2 = 0.63$), indicating that samples with lower PC1 scores had a higher contribution of less chlorinated congeners. The second principal component (PC2) was associated with the presence of the heaviest and lightest congeners, the mono- to tri- and octa- to deca- substituted congeners (Supplemental Fig. S3b).

A scatterplot of the PCA results (Fig. 4) indicated a unique congener pattern for Stege Marsh (Site ID = STEGE), in comparison to the remaining sites. When Stege Marsh was treated as an outlier and removed from the PCA, the two primary axes (PC1 and PC2) still exhibited the same qualitative patterns among the remaining data. Among the remaining sites, targeted sites generally had lower values on both axes than random sites (Fig. 4), indicating targeted sites to have a greater abundance of lower chlorinated congeners. This pattern was apparent for congener fingerprints of individual stations (Fig. 5). Stege Marsh (low scores, both axes) exhibited high concentrations of lower chlorinated congeners, reaching as high as 134 ng g^{-1} (wet weight) for PCB 52, and lower concentrations of higher chlorinated congeners (Fig. 5a). Richmond Inner Harbor (Site ID = 11OTH), another targeted site, was a less pronounced case, with high concentrations of low and high chlorinated congeners (Fig. 5c). On the opposite extreme were random sites at Suisun Marsh (25OTH) and Coyote Creek East (28OTH). Coyote Creek East (low score PC1, high score PC2; Fig. 5d) had a high relative abundance of higher chlorinated congeners, but still exhibited elevated lower chlorinated congeners compared to other ambient sites (e.g., Suisun Marsh; high PC1; Fig. 5b). One site (Seaplane Harbor near Alameda Naval Air Station; SEAPL) showed a high contribution (7.9 ng g^{-1}) of PCB 209 to the congener profile.

4. Discussion

4.1. Silversides and topsmelt as PCB biosentinels

PCB concentrations in randomly sampled San Francisco Bay forage fish (silversides and topsmelt) were similar to or higher than concentrations in the most contaminated San Francisco Bay sport fish. The average Σ40 PCB concentration in topsmelt and silverside from probabilistic stations in 2010 (115 ng g^{-1} wet weight) was similar to average 2009 concentrations in shiner perch (*Cymatogaster aggregata*; 121 ng g^{-1}; whole body minus tail, head, and digestive tract), white croaker (*Genyonemus lineatus*; 144 ng g^{-1}; skin-on fillet), and Northern anchovy (*Engraulis mordax*; 118 ng g^{-1}; skin-on fillet), and 5–12 times higher than five additional sport fish species (Davis et al., 2011). The highest Σ40 PCB concentration measured (1132 ng g^{-1} at South Basin Hunters Point) was 40–100 times the average concentrations of large predatory sport fish, including striped bass (*Morone saxatilis*, 30 ng g^{-1}), California halibut (*Paralichthys californicus*, 18 ng g^{-1}), and white sturgeon (*Acipenser transmontanus*, 11 ng g^{-1}) (Davis et al., 2011). These findings indicate that large body size and high trophic position are not positively associated with increased PCB contamination in San Francisco Bay fish.

The high tissue concentrations at industrial sites, and the strong correlation between tissue and sediment contamination, suggest that forage fish had high concentrations due to their relatively small home ranges and proximity to contaminated sediments and historic sources (Melwani et al., 2009). Sediment contamination strongly correlated with forage fish concentrations in this study, and spatial variation among sites was much more pronounced for small fish than the variation observed for sport fish (Davis et al., 2002, 2011). The elevated concentrations in topsmelt and silverside may also be partially attributable their moderately high lipid contents, as lipid affects bioaccumulation of hydrophobic contaminants, including PCBs (Kidd et al., 1998; Jarvis et al., 2008).

Previous research has supported the use of Mississippi silverside and topsmelt as biosentinels for spatial and temporal patterns in mercury contamination (Suchanek et al., 2008; Greenfield and Jahn, 2010). Our results supported the general utility of these species as biosentinels of localized PCB exposure, in that they exhibited elevated concentrations and unique congener patterns in proximity to contaminated sites. PCB average levels were threefold higher in fish collected from sites targeted for historical PCB contamination than randomly selected sites reflecting ambient Bay conditions. At areas with high levels of sediment PCBs, small fish tissue levels were also increased. Thus, the small fish indicated biotic exposure to conditions at the locations studied, including historical PCB contamination.

Based on BSAF calculations, topsmelt and silverside exhibited typical bioaccumulation in comparison to other fish species monitored globally. Calculated BSAFs (median 3.2–4.2) were lower than several piscivorous or benthivorous species, including European eel (*Anguilla anguilla*; benthivorous; BSAF range = 13–16), roach (*Rutilus rutilus*; benthivorous; BSAF range = 5–37), white croaker (*G. lineatus*; benthivorous and piscivorous; average BSAF = 5), pike (*Esox lucius*; piscivorous; BSAF range = 18–35), and kelp bass (*Paralabrax clathratus*; piscivorous; average BSAF = 27) (van der Oost et al., 2003; Melwani et al., 2009). However, topsmelt and silverside median BSAFs were higher than 10 of 15 fish species compiled in van der Oost et al. (2003, Table 1, Sum PCBs column). The significant statistical association with sediments (Fig. 3) and moderately high BSAFs exhibited by topsmelt and silverside, both benthopelagic invertivores, is interesting, considering their limited dietary sediment linkage and low trophic position. These results support the interpretation of in-bay contaminated sites and legacy sediments playing a primary role in biota pollution exposure in San Francisco Bay (Davis et al., 2007).

PCBs in topsmelt were generally higher than in silversides; however, silversides have higher mercury concentrations (Greenfield and Jahn, 2010). The higher PCBs in topsmelt was attributable to their higher lipid content (Kidd et al., 1998), evident in the fact that silversides exhibited higher BSAF (performed on lipid normalized data) than topsmelt. Although silverside and topsmelt both inhabit nearshore areas and exhibit limited movement ranges, enabling overlapping capture in many locations, subtle habitat differences reviewed in Greenfield and Jahn (2010) may explain contrasting PCB and mercury contamination between the species. Silversides favor less saline waters than topsmelt, and their distribution corresponds to the less urbanized San Pablo Bay and Suisun Bay locations (Fig. 1), where PCB contamination was reduced. Habitat differences between the species may also explain the stronger statistical association with sediment concentrations, and the lower range in BSAF, for topsmelt. Related to their salinity preferences, silverside spend more time in fringing marshes and channels draining into the Bay, and less time near the subtidal areas where sediment contamination has predominantly been monitored.

4.2. Hazards to fish and piscivorous wildlife

PCB concentrations and dioxin TEQs in most samples collected in this study exceeded thresholds for potential effects to fish and wildlife. Multiple thresholds were exceeded, sometimes by many-fold, indicating potential hazard to aquatic organisms residing within San Francisco Bay. These thresholds were developed using conservative assumptions, such as being based on the toxic response or NOAEC of sensitive wildlife, sublethal endpoints and biomarkers, development for sensitive life stages, and a lack of evaluation of population outcomes (Elonen et al., 1998; Kannan et al., 2000). Further, particularly for the targeted sites, threshold comparison implies that piscivores consume prey largely at the sites, rather than migrating off site to less contaminated locations. Taken in isolation, the present indication of potential hazard cannot be inferred to indicate the extent of risk to San Francisco Bay fish or piscivorous wildlife, or even definitively establish adverse effects, for which more detailed study would be required (Hope, 2009). However, these results do corroborate local field and modeling studies indicating sufficient PCB exposure to cause sublethal effects to local fish and piscivorous wildlife (Spies and Rice, 1988; Neale et al., 2005; Davis et al., 2007; Brar et al., 2010; Gobas and Arnot, 2010). In particular, Brar et al. (2010) indicate a statistical correlation between hepatic PCB concentrations and thyroid endocrine response in shiner perch and staghorn sculpin (*Leptocottus armatus*). In our study, fish concentrations at multiple targeted locations (Hunters Point South Basin, Richmond Inner Harbor, San Leandro Harbor, and Stege Marsh; Table 1) were at or above fish concentrations at the affected locations in Brar et al. (2010) (Oakland Harbor and San Leandro Bay). This suggests a risk of sublethal effects due to PCB exposure in multiple San Francisco Bay industrial locations. In combination with the slow recovery rate of PCB contamination (Davis et al., 2007), these findings indicate continuing hazards to San Francisco Bay fish and wildlife.

4.3. Spatial patterns

Unlike prior examinations of PCBs in aquatic biota, our study emphasized the detailed spatial patterns within a single estuary. Two general patterns were discerned: both site type and distance from Guadalupe River influenced forage fish PCB concentrations. Fish concentrations also reflected general Bay-wide spatial trends in sediment PCB concentrations, with elevated fish concentrations at targeted locations with contaminated sediments. The clear distinction between fish from targeted and non-targeted sites suggests that PCB exposure at the base of the food web remains elevated in historically contaminated areas, despite ongoing efforts to remediate PCB contamination in these hotspots (Cho et al., 1999; Davis et al., 2007).

After accounting for elevated concentrations in targeted sites, predominantly located in Central Bay, small fish PCB concentrations declined northward from South Bay through Suisun Bay. This spatial trend indicated a broad gradient in biota PCB contamination throughout the Bay. A similar pattern is seen for PBDEs and Hg in the Bay (Oros et al., 2005; Greenfield and Jahn, 2010), and studies in other industrialized water bodies also demonstrate spatial gradients of decreased fish PCB contamination with increasing capture distance from contaminated locations (Barron et al., 2000; Fernandez et al., 2004). The spatial trend of pollution declining from the South Bay likely results from changes in two attributes: extent of watershed urbanization and fluvial flushing rates (Conomos, 1979). Higher ambient sediment and forage fish PCBs in the South Bay is primarily linked to river and stormwater runoff dominated by urban and industrial regions as well as a higher residence time for water in the South Bay compared with the North Bay. The North Bay tributaries contain extensive agricultural and undeveloped land, contributing more dilute loads. Additionally the San Joaquin and Sacramento Rivers that drain into Suisun Bay have high flow volumes, which would more readily flush out legacy contamination.

Although there was a general spatial trend with distance from the Guadalupe River, forage fish PCB concentrations were also elevated in historically contaminated locations, including several Central Bay sites. The sites with the highest fish PCB concentrations have well-documented histories of PCB use and contamination in sediment. Our results indicate that multiple in-Bay and watershed sources together, rather than a single point source, contribute to increased overall exposure to Bay biota.

4.4. Congener patterns

The high variability explained by PC1, and its high correlation to congener weight, indicated that a primary factor in the variation between sites is the contribution of light versus heavy congeners. In general, targeted sites had a greater abundance of lower chlorinated congeners. Sites having lower scores for PC1 exhibit chlorination patterns characteristic of Aroclor mixture 1248. Since these congeners are more readily volatilized and degraded, their relative contribution is reduced for random sites not near legacy PCB sources.

Stege Marsh (Site ID = STEGE) had the most distinctive congener profile of all sites sampled, including particularly elevated tissue concentrations of PCB 52, PCB 66, and PCB 70. Given their low salinity and nearshore habitat preferences (Greenfield and Jahn, 2010) and the marine salinity offshore of that site, the silversides from Stege Marsh likely never roamed beyond the extent of the slough. The distinct profile and high concentration detected in the Stege Marsh silversides corresponded to sediment measurements and likely reflected local contamination by PCBs from Aroclor mixture 1248 (Hwang et al., 2006). Several historic sources of PCB contamination drain into Stege Marsh (Blasland Bouck and Lee Inc., 2005). A former Pacific Gas and Electric (PG&E) site adjoined the Western Storm Drain (WSD) which drains into the marsh. This site was used to store materials including electrical transformers, employing PCBs in hydraulic and dielectrical fluids. In the marsh sediment and the WSD, Aroclor 1248 was detected at an average concentration of 18.97 ng g^{-1}, followed by Aroclors 1254 and 1260 at average concentrations of 0.98 and 0.36 ng g^{-1}, respectively. Another sewer system deposited materials from the former Zeneca, Inc. pyrite cinder landfill into the Bay until the 1950s. Maximum PCB soil concentrations adjacent to the sewer pipe were 63 ng g^{-1}. It is unclear if the Stege Marsh PCB contamination largely originated from the PG&E or Zeneca sites, or other sources along the same drainage systems (Blasland Bouck and Lee Inc., 2005). Given a range of sources of PCBs and other contaminants in Stege Marsh, integrated assessments of chemical exposure and biological effects have determined this site to be highly impacted in comparison to other San Francisco Bay and reference wetlands (Hwang et al., 2006, 2008).

In addition to Stege Marsh, other targeted sites, including Richmond Inner Harbor (11OTH) and San Rafael Creek (SANRA-T, SANRA-M), also had relatively high relative contributions of lower chlorinated congeners. Aroclor mixtures 1016, 1242 and 1248 are discernible by the high relative contributions of PCBs 17, 18, 28, 31, 33, 44, 49, 66, and 70 (Frame et al., 1996), and were likely predominant sources at these sites. Because lower chlorinated congeners degrade and volatilize more readily, the high concentrations seen in these samples suggest either continuous sources or high concentrations of legacy PCB contamination at these sites.

Samples collected from Oakland Inner Harbor (Site ID = OAKIH), North San Leandro Bay (NSLB), South Bay near Coyote Point South (85OTH), Petaluma Marsh (22OTH), and Napa River (26OTH) exhibited higher concentrations of PCBs 95, 99, 101, 110, and 118, suggesting Aroclor 1254 as a dominant source to these regions. Congeners 149, 170, 180, and 187 contributed more to the total sum of PCBs in the samples collected from South Basin (SOBAS), Hunters Point North (HUPTN), SF Airport (23OTH), Mission Creek Mouth (78OTH), Suisun Bay at Port Chicago (79OTH), Suisun Bay at Winter Island (83OTH), and Suisun Marsh (25OTH), suggesting Aroclors 1260 and 1262 as dominant among the PCB sources at these sites. The detection of PCB 209 at Seaplane Harbor (SEAPL) may indicate the nearby use of investment casting waxes, some of which were composed solely of decachlorinated biphenyl (SFBRWQCB, 2008).

The high abundance of lower chlorinated congeners near legacy contamination sources was similarly observed in mummichog (*Fundulus heteroclitus*) from the Hudson River Estuary and Newark Bay (Monosson et al., 2003) and multiple forage fish species in Georgia and Florida (Pulster et al., 2005). Congener PCA also distinguished fish samples among sites on the San Diego, CA, offshore coastal shelf. Hypothesized causes of variation for the Southern California samples include differences in sources and taxa-specific bioaccumulation patterns (Parnell et al., 2008). The increased light congener abundance in forage fish collected from historically contaminated locations suggests continued contamination of nearshore terrestrial areas, where light congeners may be more persistent (Fu and Wu, 2006). This finding, combined with locally elevated concentrations, indicates that legacy PCB contamination remains a concern in industrialized portions of San Francisco Bay.

5. Conclusions

We employed a stratified probabilistic sampling design to examine spatial patterns in forage fish PCB concentrations at scales of five to ten km. Small fish revealed spatial trends in PCB uptake to the aquatic food web, which corresponded with sediment PCB contamination. Across fourteen targeted locations with historic industrial activities, forage fish PCB concentrations were generally higher and there was a greater relative abundance of lower chlorinated congeners, indicating local contribution of Aroclor mixtures 1016, 1242 and 1248. This finding indicates that multiple locations within this urbanized estuary, rather than a single major hotspot, contribute to overall biota exposure. Topsmelt and silverside are consumed by piscivorous wildlife, and their PCB concentrations at targeted locations were substantially greater than previously monitored sport fish concentrations in San Francisco Bay. This result, combined with the nearshore habits of these two species and the significant association between fish and adjacent sediment, suggests that nearshore sediments adjacent to industrially polluted sites are an important reservoir of legacy PCB contamination. Thus, the well documented global reservoir of PCBs remains of potential concern for urbanized locations with historic industrial activity, such as San Francisco Bay.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.09.066.

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