Water Air Soil Pollut (2011) 222:403–419
DOI 10.1007/s11270-011-0837-2

Associations Between Dioxins/Furans and Dioxin-Like PCBs in Estuarine Sediment and Blue Crab

Johan Liebens · Carl J. Mohrherr · Natalie K. Karouna-Renier · Richard A. Snyder · K. Ranga Rao

Received: 13 August 2010 / Accepted: 13 May 2011 / Published online: 28 May 2011

Abstract The objective of the present study was to evaluate the relationships between the quantity, toxicity, and compositional profile of dioxin/furan compounds (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in estuarine sediment and in the blue crab (*Callinectes sapidus*). Sediment and blue crab samples were collected in three small urban estuaries that are in relatively close proximity to each other. Results show that differences between PCDD/F and DL-PCB mass concentrations and total toxic equivalents (TEQ) toxicity in sediments of the three estuaries are reflected in those of the blue crab. TEQs are higher in the hepatopancreas of the crabs than in the sediment, but the concentration factor is inversely proportional to the TEQ in the sediments. Congener profiles in the crabs are systematically different from those in the sediments, and the difference is more pronounced for PCDD/Fs than for DL-PCBs, possibly due to differences in metabolization rates. Compared with sediment profiles, more lesser-chlorinated PCDD/Fs that have higher TEFs accumulate in crab hepatopancreas. This selective bioaccumulation of PCDD/Fs results in a TEQ augmentation in crab hepatopancreas compared with sediments. The bioaccumulation in the blue crab is also selective for PCDD/Fs over DL-PCBs.

Keywords Dioxin/furan · PCB · TEQ · Sediment pollution · Organic pollutants · Bioaccumulation

J. Liebens (✉)
Department of Environmental Studies,
University of West Florida,
32514 University Parkway,
Pensacola, FL 32571, USA
e-mail: Liebens@uwf.edu

C. J. Mohrherr · N. K. Karouna-Renier · R. A. Snyder ·
K. R. Rao
Center for Environmental Diagnostics and Bioremediation,
University of West Florida,
32514 University Parkway,
Pensacola, FL 32571, USA

Present Address:
N. K. Karouna-Renier
Patuxent Wildlife Research Center,
U.S. Geological Survey,
Laurel, USA

1 Introduction

Dioxin/furan compounds (PCDD/Fs) are ubiquitous environmental contaminants that are very stable to chemical and microbiological degradation (Wittich 1998) and therefore persistent in the environment (Birch et al. 2007). Combustion is the major source of PCDD/Fs but many other local sources exist (Rappe 1996; Wittich 1998; Johnson et al. 2007). PCDD/Fs are fat soluble (Landi et al. 1998) and enter the human food chain because they bioaccumulate in the lipids of animal tissues (ATSDR 1998). Seventeen of the PCDD/F congeners exhibit dioxin-like toxicity (van den Berg et al. 2006). Polychlorinated biphenyl (PCBs) are also persistent organic pollutants that biomagnify as they move up through the food chain (ATSDR 2000). Twelve of the 209 PCB congeners, the dioxin-like PCBs (DL-PCBs), are structurally and conformationally similar to PCDD/Fs and exhibit dioxin-like toxicity (ATSDR 2000).

Multiple studies have shown that PCDD/Fs and DL-PCBs have harmful effects on aquatic ecosystems, and that they can ultimately affect human health (Weber et al. 2008). Currently available experimental evidence indicates that the aryl hydrocarbon receptor mediates the known physiological roles of PCDD/Fs in vertebrates (Bunger et al. 2003; Stevens and Bradfield 2008). The PCDD/Fs and dioxin-like compounds are considered to be carcinogenic to humans by International Agency for Research on Cancer (IARC 1997) and the US EPA (2010).

PCDD/Fs and DL-PCBs are very stable in soils and aquatic sediments, especially those rich in organic matter. Consequently, these media act as a reservoir for the PCDD/Fs and DL-PCBs. In aquatic environments, bottom-dwelling organisms such as crabs provide a pathway for the transfer of PCDD/Fs and DL-PCBs from sediments to humans via the foodchain. Some studies have assessed the relationships between PCDD/Fs in sediments and crabs to some extent (Jimenez et al. 1998; Sakurai et al. 2000; Suarez et al. 2005; Yunker et al. 2002) but very few studies have examined the direct associations between the toxic DL-PCBs in sediments and seafood. In a coastal lagoon with minimal human impact congener profiles of PCDD/Fs in sediments and crab (*Carcinus aestuarii*) were very similar (Jimenez et al. 1998). In an anthropogenically impacted lagoon, the same study found differences between congener profiles in sediments and crab. PCDFs were more abundant than PCDDs in the crabs as compared with the sediments, and especially 2378 TCDF had higher proportions in the crabs (Jimenez et al. 1998). Sakurai et al. (2000) found that the congener composition in crab (*Charybdis japonica*) from Tokyo Bay somewhat resembled that in nearby sediments, especially in the HxCDDs and HxCDFs. Yunker et al. (2002) concluded that PCDFs from chlorine bleaching in British Columbia accumulated more readily from sediments to Dungeness crab than did PCDDs. Compared with sediments, a greater abundance of PCDFs than PCDDs, especially the octaforms, was also observed in crab (*Callinectes sapidus*) in Houston Ship Channel (Suarez et al. 2005). The objective of our study is to help remedy the incomplete knowledge of these relationships between PCDD/Fs and DL-PCBs in sediments and crabs by evaluating the connections between the quantity, toxicity, and compositional profile of PCDD/Fs and DL-PCBs in the blue crab (*C. sapidus*) and sediments in three anthropogenically altered estuaries. Because adult blue crabs as a bottom-dwelling species are in direct contact with sediments and are less mobile than most fish species their tissue concentrations have been extensively used as indicators of sediment contamination levels (Dean et al. 2009; Iannuzzi et al. 2004; Ylitalo et al. 1999), illustrating the importance of better understanding the relationships between pollution in sediments and this crab. The use of *C. sapidus*, the blue crab, as a biomarker also highlights the need to further examine these relationships. Additionally, the connections between PCDD/F and DL-PCB concentrations in aquatic organisms and sediments is of interest when estimating human exposure to these compounds (Sakurai et al. 2000) and when assessing the ecological risk posed by these chemicals to different levels of the aquatic food web (Micheletti et al. 2007). The blue crab represents one of the largest recreational and commercial fisheries in the Gulf of Mexico, to which our study sites are hydrologically connected.

2 Materials and Methods

2.1 Study Area

The three estuaries that were sampled for this study are part of the Pensacola Bay System and are located in Northwest Florida (Fig. 1). The estuaries are fed by freshwater streams and stormwater outfalls, and receive saline waters from Pensacola Bay. Land use in the drainage basins of the three estuaries has greatly changed during the last 50 years from agriculture and silviculture to residential and commercial. Bayou Texar is currently bordered by residential neighborhoods and is affected by at least one groundwater plume from a former industrial site (Liebens et al. 2006). Bayou Chico has had a number of industrial facilities on its banks for almost a century, including chemical, scrap metal recycling, marinas, and ship building facilities. Industrial, commercial, and nonpoint pollution has severely

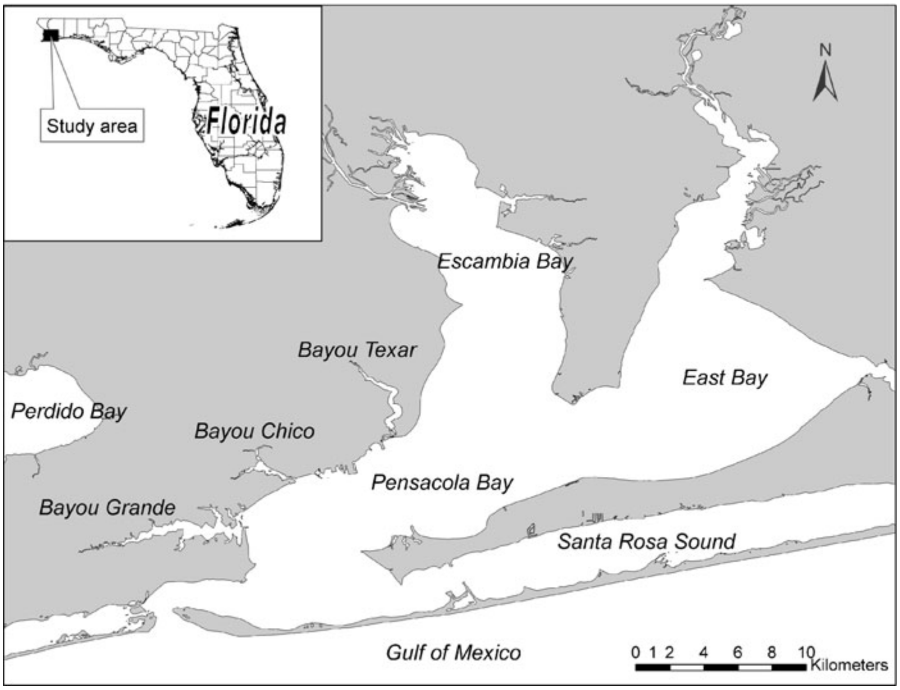

Fig. 1 Location of the three urban estuaries in northwest Florida

impacted the quality of the sediments and water of this estuary (Liebens et al. 2007). Bayou Grande still contains substantial undeveloped shoreline in its most western reaches. Its northern shoreline is bounded by civilian residences and much of the southern shore borders a military installation.

2.2 Sample Collection and Analysis

A stratified random sampling scheme was used for the sediment sampling to have approximately equal numbers of samples from deep and shallow sites in each estuary. A total of 17 sites were sampled in Bayou Chico, 13 in Bayou Texar, and 23 in Bayou Grande (Fig. 2). At each site, five local grab samples were taken with a ponar grab sampler and mixed thoroughly prior to further processing. The composited samples were placed into precleaned dedicated sampling containers, preserved on wet ice, and sent to the analytical laboratory the day of sampling. Rinsate blanks from decontaminated equipment and field splits of samples were taken for quality control. Blue crabs (*C. sapidus*) were collected at three sites in Bayou Chico, three sites in Bayou Texar, and two sites in Bayou Grande (Fig. 2). The crabs were collected with commercial traps that were deployed for 2 to 3 days at each site. Male crabs 10.2–19.3 cm in width were retained and shipped to the lab on wet ice. Seven to 15 crabs were composited for each site (Table 1). Male crabs were selected due to a tendency for greater site fidelity than females who make spawning migrations. Details of crab sample preparation are provided in Karouna-Renier et al. (2007).

All samples were analyzed for the 17 2378 substituted PCDD/Fs and the 12 DL-PCBs by commercial laboratories (Columbia Analytical, Houston, TX for sediments and Alta Analytical Perspectives, Wilmington, NC, for crabs). Analysis were performed by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC-HRMS) using US EPA method 1668A for DL-PCBs, 1613B for PCDD/Fs in sediments, and 8290B for PCDD/Fs in crab tissue (US EPA 2009). Quality assurance/quality control (QA/QC) measures included analysis of method blanks, duplicate samples, matrix spikes, and laboratory control samples. All laboratory QA/QC procedures had results within acceptable limits as specified in National Environmental Laboratories Accreditation Program guidelines. Average congener detection limits for crab samples were between 0.03 and 0.25 ng/kg for PCDD/Fs and 0.03 to 0.15 ng/kg for DL-PCBs. For sediments, average detection limits for individual congeners were between 0.180 and 1.813 ng/kg for

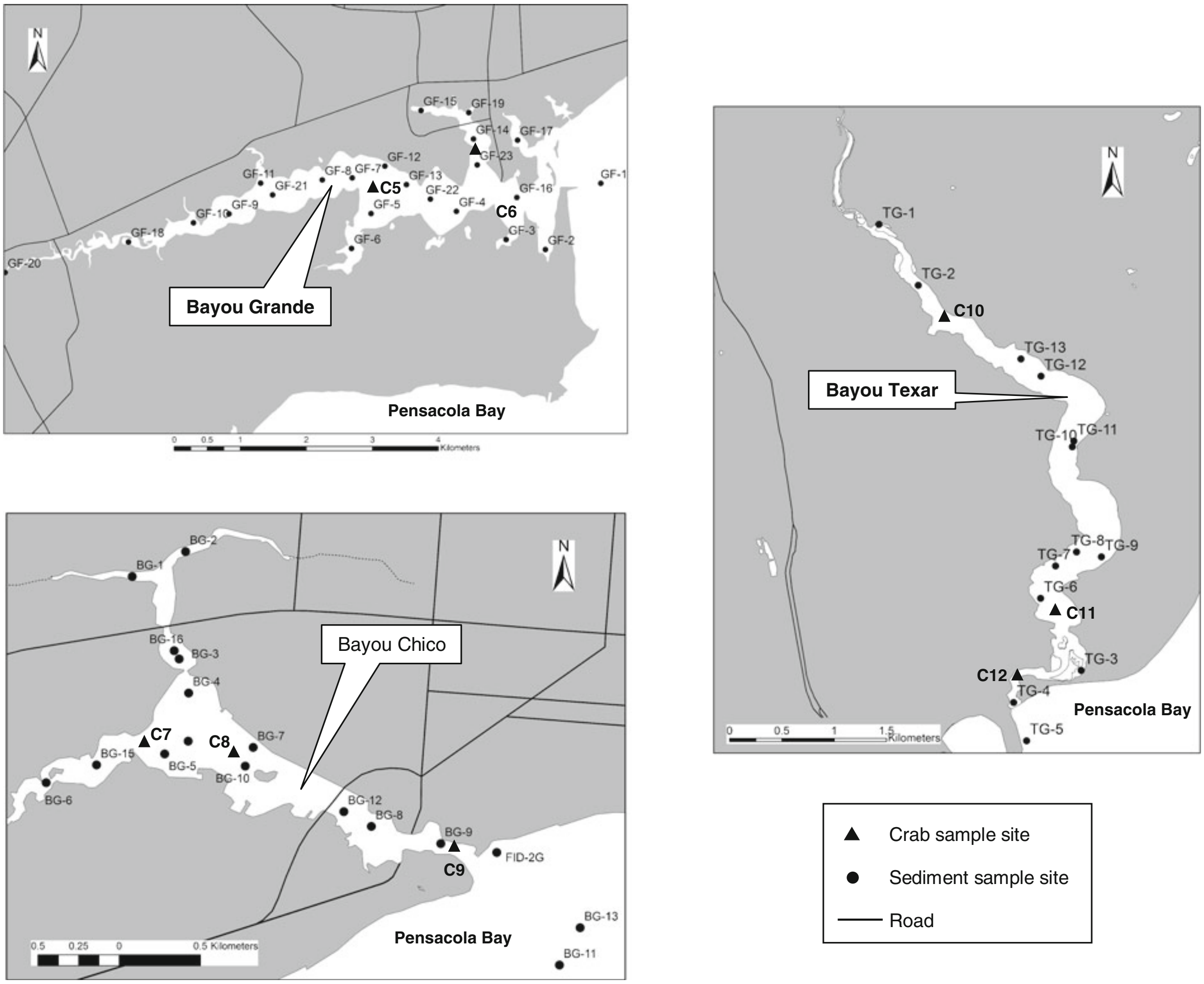

Fig. 2 Location of crab and sediment sampling sites in the three estuaries

Table 1 Crab collection data

Sample location[a]	Number of crabs	Date
Bayou Grande		
C5	7	October 2003
C6	7	October 2003
Bayou Chico		
C7	8	September, October, December 2003
C8	7	September, October, December 2003
C9	7	September, October 2003
Bayou Texar		
C10	12	September, November 2003
C11	10	September 2003
C12	7	September 2003

[a] See Fig. 2 for location of crab samples

PCDD/Fs and between 2.08 and 6.80 ng/kg for DL-PCBs. Analytical results for sediments were on a dry weight basis, those for crab were on a wet weight basis. For comparative purposes, we converted wet weight based concentrations for crabs to dry weight based with a conversion factor of 17% (Lewis et al. 2004).

2.3 Calculations

To best determine the potential environmental impact of the PCDD/Fs and DL-PCBs we determined the total toxic equivalents (TEQ) for both groups of analytes separately and combined (US EPA 2003). The TEF values for humans/mammals established in 2005 by the World Health Organization (van den Berg et al. 2006) were used for the TEQ calculation. Half the detection limit was substituted for analytical results below the detection limit (BDL). Two PCDD/F congeners (2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF) were omitted from the calculations because their analytical result was BDL for more than half of the samples. Some studies have standardized PCDD/F concentrations with sediment organic carbon content but several have found little influence of standardization on results (Bonn 1998; Foster et al. 1999). We applied a principal component analysis (PCA) to our dataset as an ordination tool to examine if statistical similarities exist in the congener profiles of individual sediment and crab samples. We used the relative proportion of each congener with respect to the total concentration in each sample to represent the profiles rather than the absolute values of the congeners. This also minimizes bias due to large differences in concentrations between samples and congeners (Lake et al. 1995; Rachdawong and Christensen 1997; Wenning et al. 1993). We used the samples as variables and congener proportion as cases because we were interested in assessing communality in the samples (Rachdawong and Christensen 1997). We used the correlation matrix for extraction of the components, and applied a varimax rotation, which simplifies interpretation of the components (Peré-Trepat et al. 2006). Only factors with an eigenvalue of >1 were retained.

To assess relationships between crab samples and nearby sediments we applied an inverse distance-weighted spatial interpolation (IDW) to the sediment data in a geographic information system. This created an interpolated continuous surface for the various sediment data in each of the estuaries. We used a power of three for the IDW to limit the spatial influence each sediment site has on far away locations to mimic the limited range of the male crabs that were collected. Data for sediments at the crab sample sites were then obtained with a spatial overlay of the interpolated surfaces and the crab sample locations.

3 Results and Discussion

3.1 Mass Concentrations in Blue Crab Versus Sediments

Sediments have much higher total PCDD/F mass concentrations in Bayou Chico (geometric mean of 5,207 ng/kg) than in the other two bayous, and roughly comparable concentrations in Bayous Grande and Texar (geometric means of 797.1 and 823.0 ng/kg, respectively) (Table 2). Crab samples have lower PCDD/F mass concentrations than the sediments but the pattern observed in the sediments, highest in Bayou Chico and lower but comparable in the other two estuaries, is mirrored in the crab samples (Table 2). The pattern can be explained by differences in land use surrounding the estuaries. The industry has been present on the banks of Bayou Chico for about a century, but bayous Grande and Texar are surrounded mostly by urban areas.

The geometric mean total mass concentrations of the DL-PCBs for both types of tissue are highest in Bayou Chico (175,161 ng/kg for HP and 3,455 ng/kg for muscle), as is the case for the sediments. The Spearman's correlation coefficient between the average mass concentration for the sediments at the crab sampling sites as determined by IDW interpolation and the mass concentration in the respective crab muscle is high for both PCDD/Fs (r=0.60, n=8) and DL-PCBs (r=0.62, n=8). In HP, the correlation coefficient is intermediate (r=0.52 and 0.38 for PCDD/F and DL-PCBs, respectively, n=8). These observations point to the sediments as a direct or indirect source for these pollutants in blue crab. To our knowledge, few studies have reported on the associations between DL-PCB concentrations for sediments and crab HP. The full suite of PCBs was analyzed in sediments and blue crab from Houston Ship Channel (Howell et al. 2008) but individual DL-PCB congener data were not published. Correlation analysis for the full suite of PCBs from that study

Table 2 PCDD/F and DL-PCB concentrations[a] and TEQ (ng/kg) for sediments and crab samples

	Total PCDD	Total PCDF	Total PCDD/F	TEQ[b] PCDD/F	Total DL-PCB	TEQ[b] DL-PCB	TEQ[c] Total
Sediments							
Median BG[d]	1,352	51.0	1,404	5.1	648.0	1.5	8.7
Geomean BG[e]	772.3	23.6	797.1	2.6	783.0	1.2	5.0
Min BG	52.54	1.3	53.8	0.2	62.6	0.1	0.5
Max BG	3,544	97.9	3,624	10.9	15,345	11.7	18.1
Median BC[d]	10,568	310.3	11,020	32.7	1,412	1.0	34.6
Geomean BC	4,841	171.4	5,207	15.8	1,186	0.8	18.4
Min BC	18.35	1.49	19.8	0.2	21.3	<0.1	0.3
Max BC	60,134	1,135	60,825	129.3	23,543	21.7	145.5
Median BT[d]	725.9	31.2	754.3	2.4	717.0	0.2	2.7
Geomean BT	784.9	36.8	823.0	2.3	584.3	0.3	2.7
Min BT	156.3	6.2	162.5	0.3	53.6	0.02	0.3
Max BT	2,969.4	110.7	3,072	7.4	1,650	4.2	10.3
Median all seds.	1,781	66.0	1,872	5.9	879.6	0.7	8.6
Geomean seds.	1,430	50.9	1,502	4.6	838.1	0.7	6.7
Min all seds.	18.4	1.3	19.8	0.2	21.3	<0.1	0.3
Max all seds.	60,134	1,135	60,825	129.3	23,543	21.7	145.5
Hepatopancreas							
C5_BG	79.2	531.9	611.1	5.9	111,281	8.5	14.4
C6_BG	69.3	49.5	118.8	3.0	138,305	22.2	25.1
Median	74.2	290.7	364.9	4.4	124,793	15.3	19.8
Geomean	74.1	162.3	269.4	4.2	124,060	13.7	19.0
C7_BC	1,271	267.8	1,539	20.0	267,415	13.5	33.5
C8_BC	1,189	380.0	1,569	15.3	248,135	10.2	25.5
C9_BC	256.1	95.8	351.8	7.9	142,194	7.4	15.3
Median	1,189	267.8	1,539	15.3	248,135	10.2	25.5
Geomean	728.8	213.6	947.2	13.4	211,309	10.0	23.5
C10_BT	73.5	115.9	189.5	3.6	196,695	8.8	12.4
C11_BT	190.5	107.1	297.5	7.6	136,263	7.2	14.7
C12_BT	150.3	57.6	207.9	4.7	227,677	13.5	18.2
Median	150.3	107.1	207.9	4.7	196,695	8.8	14.7
Geomean	128.2	89.4	227.1	5.1	182,739	9.5	14.9
Median all HP	170.4	111.5	324.7	6.7	169,445	9.5	16.7
Geomean all HP	214.4	143.9	404.9	7.0	175,161	10.6	18.8
Min all HP	69.3	49.5	118.8	3.0	111,281	7.2	12.4
Max all HP	1,271	531.9	1,569	20.0	267,415	22.2	33.5
Muscle							
C5_BG	8.8	14.6	23.4	0.2	3,910	0.4	0.6
C6_BG	2.5	1.8	4.3	0.1	2,147	0.5	0.6
Median	5.6	8.2	13.8	0.2	3,028	0.4	0.6
Geomean	4.7	5.1	10.0	0.2	2,897	0.4	0.6
C7_BC	53.8	6.9	60.6	0.5	4,812	0.2	0.7
C8_BC	122.9	9.8	132.6	0.6	6,409	0.3	0.8
C9_BC	18.5	2.8	21.3	0.2	1,991	0.1	0.3

Table 2 (continued)

	Total PCDD	Total PCDF	Total PCDD/F	TEQ[b] PCDD/F	Total DL-PCB	TEQ[b] DL-PCB	TEQ[c] Total
Median	53.8	6.9	60.6	0.5	4,812	0.2	0.7
Geomean	49.6	5.7	55.5	0.4	3,946	0.2	0.5
C10_BT	6.6	3.6	10.2	0.2	5,373	0.3	0.5
C11_BT	5.6	2.2	7.8	0.1	2,930	0.2	0.3
C12_BT	1.3	1.6	2.8	01	2,504	0.1	0.2
Median	5.6	2.2	7.8	0.1	2,930	0.2	0.3
Geomean	3.6	2.3	6.1	0.1	3,403	0.2	0.3
Median all muscle	7.7	3.2	15.8	0.2	3,420	0.2	0.5
Geomean all muscle	10.3	4.0	15.8	0.2	3,455	0.2	0.4
Min all muscle	1.3	1.6	2.8	0.1	1,991	0.1	0.2
Max all muscle	122.9	14.6	132.6	0.6	6,409	0.5	0.8

[a] Units for mass concentrations are ng/kg dry weight

[b] TEQ was determined with TEFs from van den Berg et al. (2006)

[c] Total combined TEQ (TEQ total) is equal to the sum of the TEQs for PCDD/Fs and DL-PCBs for individual samples only. For other rows, it is a statistical value

[d] *BG* Bayou Grande, *BC* Bayou Chico, *BT* Bayou Texar

[e] *Geomean* geometric mean

revealed a moderate (r=0.47 and n=41) positive correlation between PCB mass concentrations in crab tissue and sediments. This correlation is roughly comparable to what we found for the DL-PCBs (r=0.38 and 0.62 for HP and muscle respectively, n=8).

3.2 TEQ in Blue Crab Versus Sediments

The geometric means for the PCDD/F TEQ in the crab HP and the sediments follow the same pattern: They are highest in Bayou Chico and lower but similar in bayous Grande and Texar (Table 2). The total combined TEQ is also higher in the HP than in the sediments of the respective estuaries (total combined TEQ geometric means of 19.0 vs. 5.0 ng/kg for Bayou Grande, 14.9 vs. 2. 7 ng/kg for Bayou Texar, and 23.5 vs. 18.4 ng/kg for Bayou Chico) (Table 2).

The concentration factor for total combined TEQ in crab HP, as expressed by the ratio of the total combined TEQ in HP and in IDW interpolated sediments at the crab sampling site, is on average 7.5. However, the concentration factor is markedly inversely proportional to the total combined TEQ in the sediments, and closely follows a negative power function (Fig. 3). This indicates that a relative upper limit exists for how much total combined TEQ can accumulate in crab HP from sediments via the multiple processes involved. The concentration factor graph (Fig. 3) shows that, as a result of this limitation, biomagnification of total combined TEQ in crab HP is minimal above a total combined TEQ in sediments of about 20 ng/kg. This may be the result of a diminishing rate response increase as PCDD/F and DL-PCB concentrations increase. It is also possible that the crabs avoid the most contaminated areas for feeding or that these areas may not have a lot of food for the crabs. These findings are important for TEQ monitoring efforts because sediment TEQ is sometimes used as a proxy for biota TEQ.

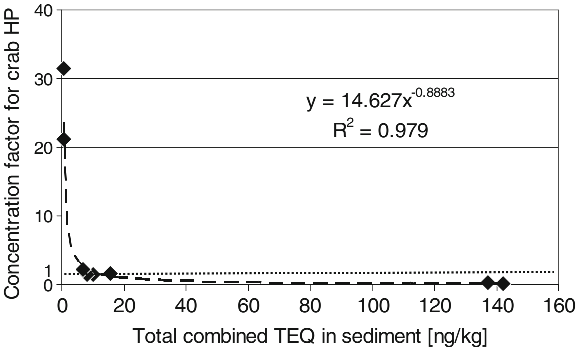

Fig. 3 Concentration factor for total combined TEQ for crab HP relative to sediments

The contributions from the various congeners to total combined TEQ in crab is very similar for HP and muscle (r=0.99, n=28) (Fig. 4). The highest contribution to total combined TEQ in the crab samples is from DL-PCB 126 in all three estuaries (Fig. 4). The high contribution is due to the congener's high TEF compared with other PCBs and high concentration compared with the PCDD/Fs, and occurs in spite of its metabolizing rate that is higher than that of other PCBs (Micheletti et al. 2008; Van der Linde et al. 2001). 2378 TCDD and 12378 PeCDD have the next highest contributions to TEQ in crab samples, mainly due to their high TEFs. For sediments DL-PCB congener 126 is also the main contributor to total combined TEQ in Bayou Grande (Fig. 4a), but in bayous Chico and Texar 1234678 HpCDD is the main contributor to total combined TEQ (Fig. 4b, c). This PCDD's high influence is mainly due to its relatively

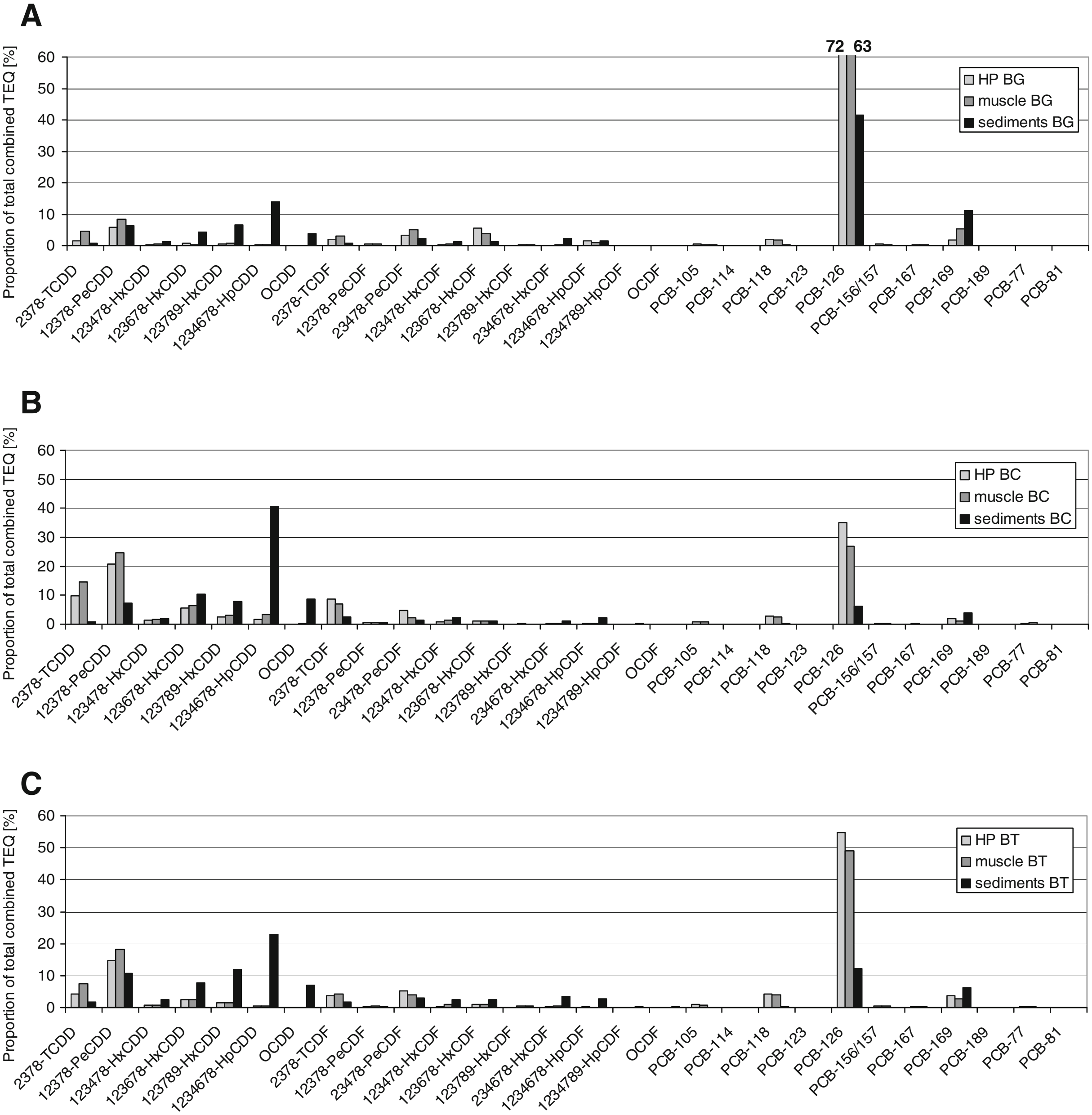

Fig. 4 Contribution (%) of individual congeners to total combined TEQ. **a** Bayou Grande; **b** Bayou Chico; **c** Bayou Texar

high mass concentration in these estuaries. Secondary influences on total combined TEQ in sediments are from 12378 PeCDD, 123789 HxCDD, 123678 HxCDD, and DL-PCB 169, but the order of their influence varies between estuaries (Fig. 4). In any case, DL-PCB 126 and 2378 TCDD and 12378 PeCDD have much larger contributions to total combined TEQ in crab than in sediments, and 1234678 HpCDD is a much greater contributor in sediments. Only two of the DL-PCBs have considerable contributions to total combined TEQ (DL-PCB 126 and DL-PCB 169) and overall the DL-PCBs are a larger contributor to total combined TEQ in crab than in sediments (Fig. 4).

3.3 PCDD/F and DL-PCB Congener Profiles

3.3.1 Congener Profiles in Sediments

The average PCDD/F congener profiles for the three estuaries have some common characteristics (Fig. 5). OCDD is the most common congener and represents between 84.7% (Bayou Grande) and 87.2% (Bayou Chico) of the total PCDD/F concentration. A similar proportion (85%) was found for OCDD in 2378 substituted PCDD/Fs in the Houston Ship Channel (Suarez et al. 2005). The second most common congener in the present study is 1234678 HpCDD (between 8.4% and 11.5%). The furan with the highest concentration is also the octaform (OCDF) with proportions being between 1.4% (Bayou Grande) and 3.0% (Bayou Texar). 1234678 HpCDF is the second most abundant furan with proportions ranging from 0.8% (Bayou Chico) to 1.0% (Bayou Texar) (Fig. 5). The most common DL-PCB is congener 118 that ranges from 54.0% (Bayou Grande) to 62.5% (Bayou Chico) of the total DL-PCB concentration (Fig. 6). The dominance of this congener may be due to its higher prevalence in aroclors than the other DL-PCBs, especially in aroclor 1254 (7.35% to 13.69% PCB118) (Frame et al. 1996) which is one of the

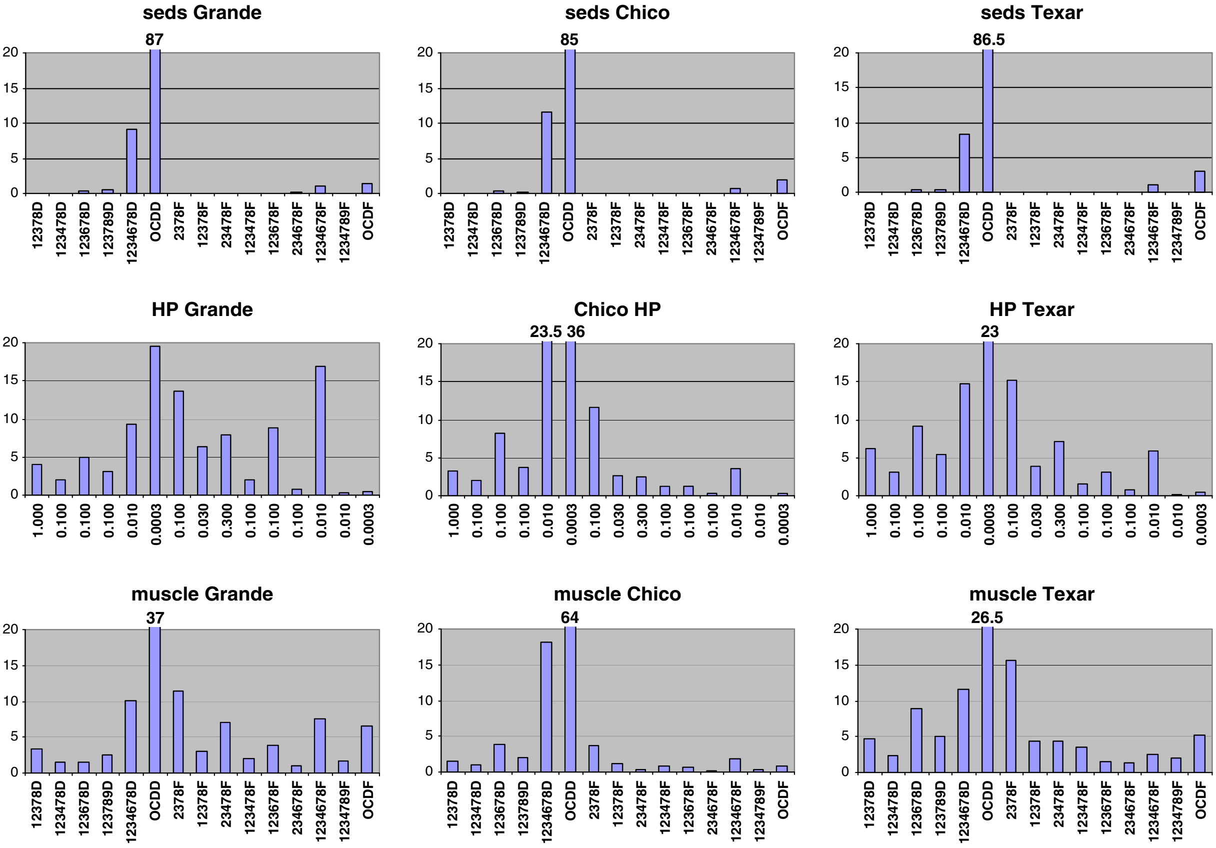

Fig. 5 Average PCDD/F profiles for sediments, HP, and muscle in the three estuaries. Relative proportion on y-axis is in %. x-Axis labels on HP graphs are TEF values

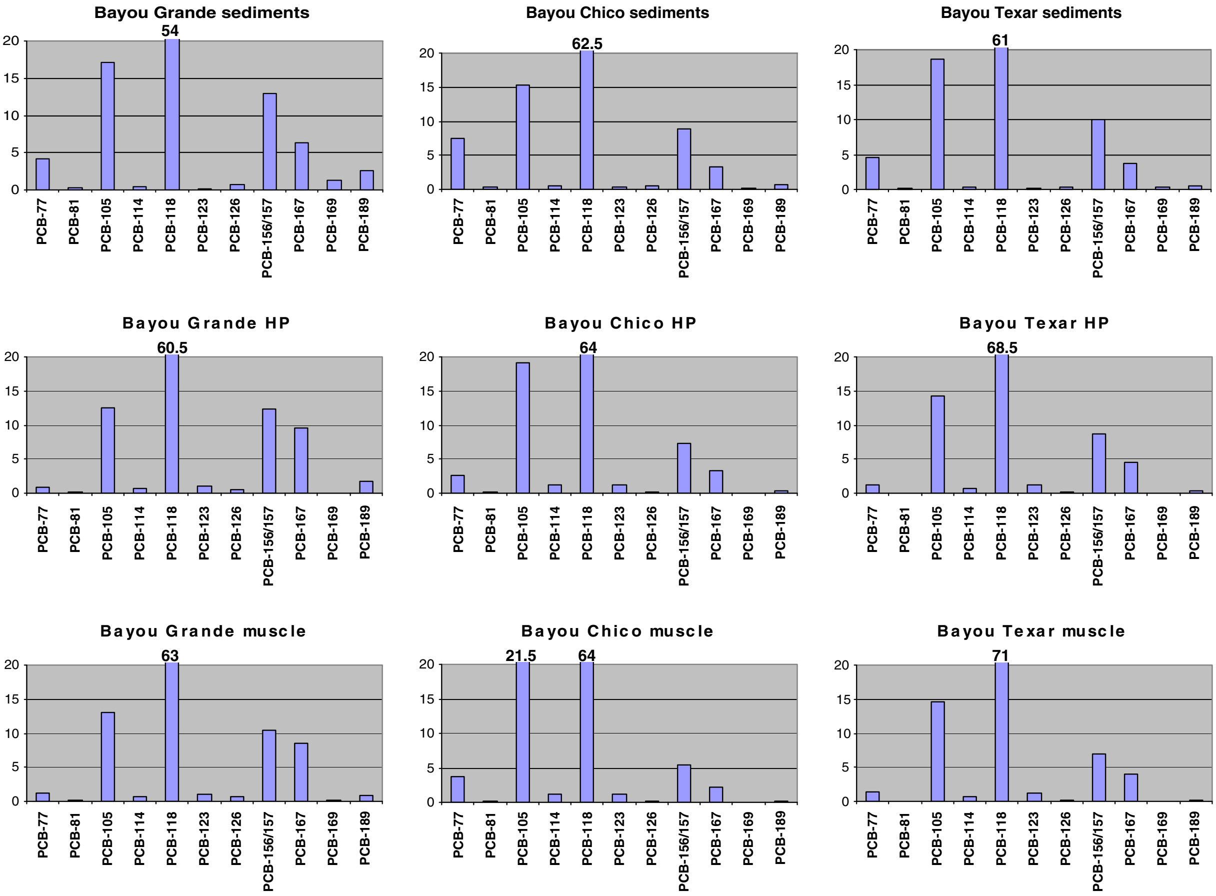

Fig. 6 Average DL-PCB profiles for sediments, HP, and muscle in the three estuaries. Relative proportion on *y*-axis is in %

more common aroclors in the environment. The dominance is probably not due to higher resistance to environmental degradation since the half life of congener 118 is about midrange when compared with that of other DL-PCBs (Sinkkonen and Paasivirta 2000). Congener 105, the second most abundant PCB, has proportions between 15.4% (Bayou Chico) and 18.7% (Bayou Texar).

3.3.2 Congener Profiles in Blue Crab Versus Sediments

The PCDD/F congeners for the crab HP and muscle are more evenly distributed than those for the sediments (Fig. 5). The more fully chlorinated congeners OCDD and OCDF have lower proportions in the crab samples than in the sediments and the lesser-chlorinated congeners have higher proportions. OCDD is still the most common congener but the average proportion is much lower (27.9% for HP and 45.6% for muscle) than in sediments (85% to 87%). 1234678 HpCDD is still the second most common congener but has higher average proportions (16.6% for HP and 15.0% for muscle) than in sediments. OCDF and 1234678 HpCDF, which had the highest PCDF proportions in sediments, are exceeded by several other, lesser-chlorinated PCDF congeners in the crab samples (Fig. 5). This is similar to what was noted in Venice Lagoon (Jimenez et al. 1998), and for OCDF has been explained by low bioaccumulation rates (Yunker and Cretney 2000). Also, the octanol–water partition coefficients (K_{ow}) for OCDD and OCDF is higher than for other dioxins and DL-PCBs (Micheletti et al. 2008). It is also possible, yet unproven, that there are some membranal processes relative to assimilation of these more chlorinated forms that are not completely dominated by K_{ow}. Additionally, metabolism of PCDD/PCDFs may degrade OCDD and OCDF and if this process is rapid enough may result in less total accumulation of these more fully chlorinated congeners (Micheletti et al. 2008; Van der Linde et al. 2001). This is consistent with the relative increase in the present study of for instance TCDD in crabs compared with sediments. Our observations indicate that the crabs do not bioaccumulate the various PCDD/F congeners in the proportion that they are present in the sediment. 2378 TCDF, for example, is present in very small proportions in the sediments but is the third most common congener in the blue crab samples. A similar increase of 2378 TCDF in crab compared with sediments has been observed in Venice Lagoon (Jimenez et al. 1998). Proportions of OCDD and 2378 TCDF in our crab samples are more consistent with those of crustaceans in "clean" areas than in "polluted" areas (Bodin et al. 2007). The congener profiles for crab muscle are similar to those for HP (Fig. 5), but observations for crab muscle have to be interpreted with caution because concentrations were generally low in crab muscle and some analytical results, i.e., those between the detection limit and the reporting limit, had to be estimated.

Comparison of the PCDD/F congener profiles of the HP samples with those of the sediments from the same estuary shows that the congeners with the highest TEFs, 12378 PeCDD (TEF=1.0) and 23478 PeCDF (TEF=0.3), have higher proportions in the HP than in the sediments while the most completely chlorinated congeners with the lowest TEFs, OCDD (TEF=0.0003) and OCDF (TEF=0.0003), have lower proportions in the HP (Fig. 5). These observations indicate that congeners with higher TEFs have higher proportions in the HP, and thus, the HP has a higher PCDD/F TEQ per unit mass concentration than the sediments. Even though crab muscle has congener profiles that are generally similar to those for HP, this TEQ augmentation is not as pronounced in muscle because OCDD and OCDF have somewhat higher proportions in muscle than in HP. Few studies have reported on this TEQ augmentation, but in Tokyo Bay edible portions of crab also have higher proportions of high TEF congeners (12378 PeCDD and 23478 PeCDF) and lower proportions of low TEF congeners (OCDD and OCDF) than nearby sediments (Sakurai et al. 2000), as is observed in the present study. A related observation has been made for fish tissue, in which the toxic 2378 substituted congeners were found to accumulate more than the less toxic congeners (Bonn 1998; Sakurai et al. 1996). The lower accumulation of higher chlorinated congeners, such as OCDD and OCDF, observed in the current study has been found before in fish (Bonn 1998; Foster et al. 1999; Sakurai et al. 2000) and some marine food webs (Ruus et al. 2006), but has rarely been reported on in blue crab. Similar findings have been postulated as due to reduced membrane permeability and possibly slow transport through intestinal aqueous phases because of low aqueous solubility (Dean et al. 2009; Ruus et al. 2006), but there do not appear to be direct experimental data to support this postulation. In principle, additional sources of PCDD/Fs could explain a change in congener profile. However, the ingestion of detritus and sand grains has been reported in a feeding study of blue crabs from nearby Apalachicola Estuary (Laughlin 1982) and it is common for these crabs to bury themselves in sediment while pumping water through their gill chambers. Therefore, input of sedimentary PCDD/Fs must affect blue crab significantly. Direct input from water is unlikely to be a major source of PCDD/Fs for the blue crab given the low water solubility of PCDD/Fs. Pelagic food and suspended sediments could in principle be additional sources but it has been shown that in the absence of a large current supply of PCDD/Fs, as is the case in the estuaries in the present study, PCDD/F uptake from these sources by crabs is very small (Yunker et al. 2002).

The DL-PCB profiles in crabs are similar to those for the sediments (Fig. 6), an observation made for muscle from other crustaceans elsewhere (Bodin et al. 2007). Spearman's correlations between average DL-PCB profiles in sediments and crab samples range from 0.76 for sediments and HP in Bayou Texar to 0.92 for sediments and HP in Bayou Chico (n=11). The DL-PCB profiles are more similar to those for the sediments than the PCDD/F profiles in crabs (Fig. 5). This can be explained by the higher accumulation efficiencies of DL-PCBs compared with PCDD/Fs (Bright et al. 1995; Lundebye et al. 2004; Micheletti et al. 2007). Congener 118 is the most abundant DL-PCB with average proportions of 65.7% of the total DL-PCB concentration in crab HP and 67.5% in crab muscle. Congener 105, the second most abundant DL-PCB in the crab samples has proportions of

15.6% and 16.7% for HP and muscle, respectively. The high proportions of these two congeners in crabs from the three estuaries is consistent with findings along the East Coast of the USA where similar proportions were observed for blue crab HP (Ylitalo et al. 1999). PCB congeners 77 and 169 have lower proportions in crabs than in sediments, most likely due to the metabolizing nature of these two congeners (Micheletti et al. 2008; Van der Linde et al. 2001).

3.3.3 Principal Component Analysis

Average congener profiles can mask spatial variations in the profiles and may conceal local relationships between the profiles of sediments and biological samples. Therefore, we used PCA on our complete dataset of PCDD/Fs and DL-PCBs to determine if statistical similarities exist in the congener profiles of individual sediment and crab samples. The PCA results gave two factors with an eigenvalue of >1. After varimax rotation these two factors explained 97.7% of the variance, showing that these factors almost completely describe the dataset. A PCA loadings plot shows that the sediments from the three estuaries are mostly separated along a curve but that some overlap exists between the sediments from Bayou Grande and the other two estuaries (Fig. 7). This implies that the sediments from the three estuaries have different congener profiles but that some overlap exists. This pattern can be explained by the fact that the estuaries are affected by both regional and local sources of PCDD/Fs and DL-PCBs. Potential regional sources for PCDD/Fs include various types of combustion and subsequent aerial deposition, local sources include the military facility on the south shore of Bayou Grande where PCDD/Fs have been detected, wood treating materials possibly contributing PCDD/Fs to Bayou Texar, and multiple sources for PCBs in Bayou Chico (Mohrherr et al. 2006). Two sediment samples taken in Pensacola Bay just outside Bayou Chico plot far outside the range of the other sediment samples (Fig. 7) because they have very different component loadings. Given that the loadings reflect communality in the congener profile, the graph indicates that these two samples have profiles that are different from those of the other sediments. The difference in profiles suggests that these two samples in the bay have either a different source of PCDD/Fs and DL-PCBs than the estuaries or that they originated in Bayou Chico but underwent advanced differential decomposition due to a greater age, which may be attributable to the time required for transport out of the bayou.

The crab samples are clustered in one region of the loadings plot (Fig. 7) and are well separated from the sediment samples, indicating that all crab samples have similar congener profiles that are distinct from those of any of the sediments. This shows that the biological processes that affect the profile of PCDD/Fs and DL-PCBs in crab HP and muscle systematically

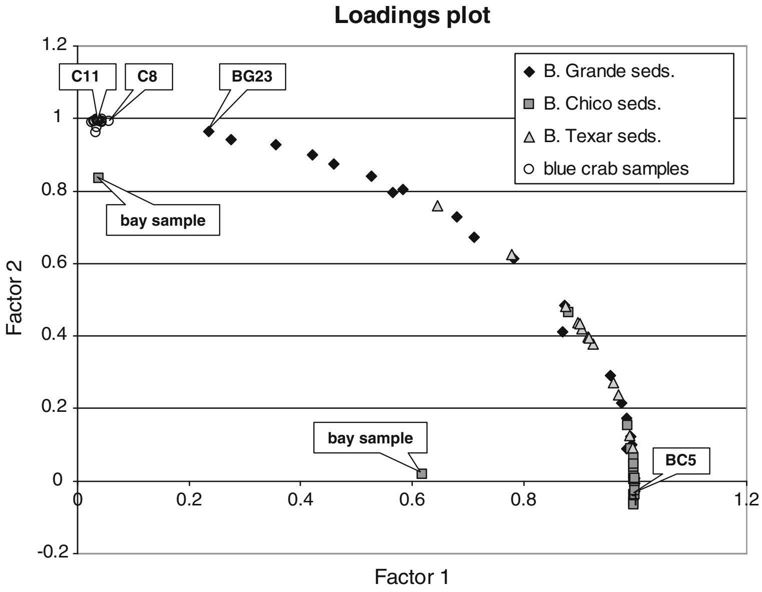

Fig. 7 PCA loadings plot for PCDD/Fs and DL-PCBs for sediment and crab samples

shift the original congener profiles of the sediments in producing the final profiles detected in crabs. Comparison of the average profiles for sediments, HP and muscle suggests that the separation in the loading plot is due to a higher proportion of DL-PCBs in the crab samples (Fig. 8). This is corroborated by comparison of profiles for individual samples from various parts of the loading plot (Fig. 9) and indicate that the processes involved in bioaccumulation in blue crab are also selective for PCDD/Fs versus DL-PCBs. HP sample C11 is from near the center of the cluster of crab samples on the loading plot and has very low proportions of PCDD/Fs (Fig. 9a). The muscle sample C8 is the crab sample that is closest to the sediment samples in the loadings plot and has somewhat higher but still very low proportions of PCDD/Fs (Fig. 9b). Sediment sample BG23 is the sediment sample closest to the cluster of crab samples in the loading plot (Fig. 7) and has yet higher proportions of PCDD/Fs (Fig. 9c). Sediment sample BC5 is from the opposite end of the loadings plot and has a high proportion of PCDD/Fs and low proportion of DL-PCBs (Fig. 9d). This comparison shows that the trend of the loadings plot from the upper left to the lower right of the graph represents a shift in the profile from a dominance of DL-PCBs to a dominance of PCDD/Fs with a distinct break between the crab and the sediment samples. The high proportions of DL-PCBs in the crab samples do not substantially influence the TEQ because of their very low TEFs compared with the PCDD/Fs.

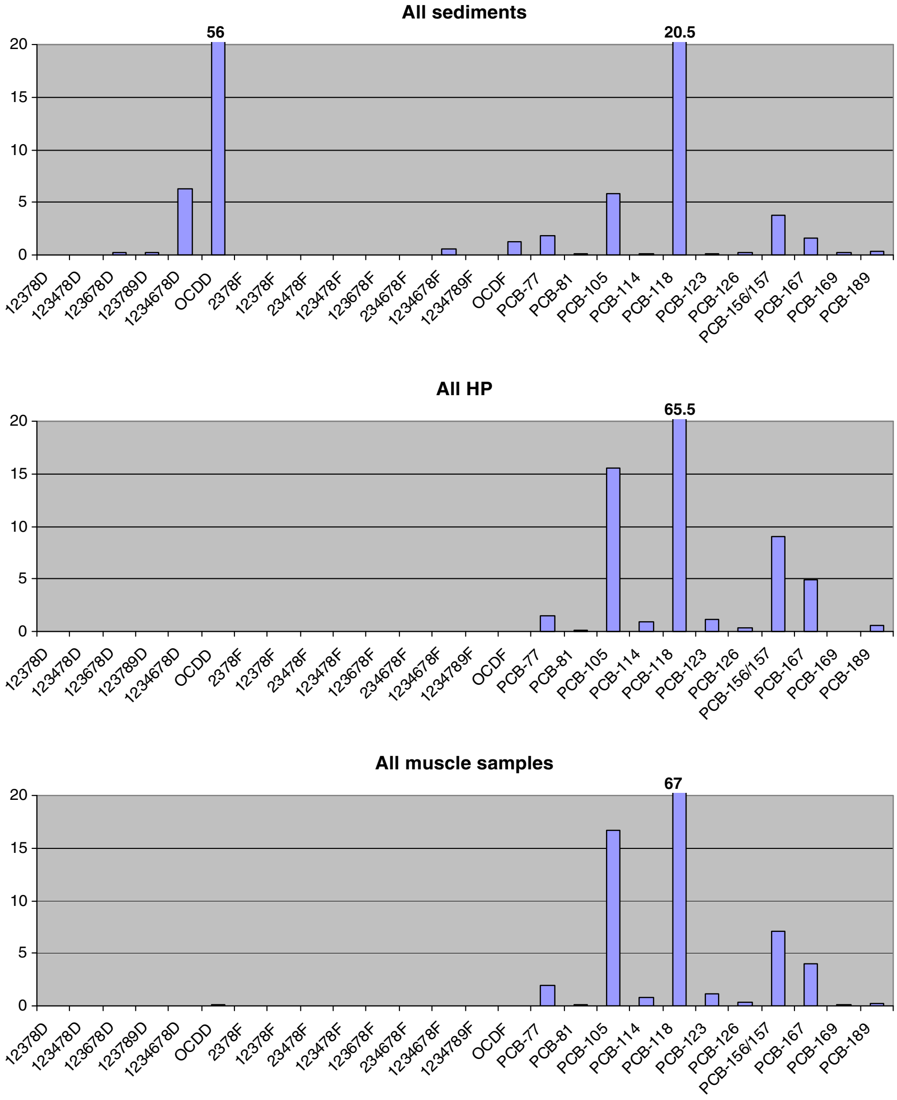

Fig. 8 Average PCDD/F and DL-PCB congener profiles as % of total combined mass concentration

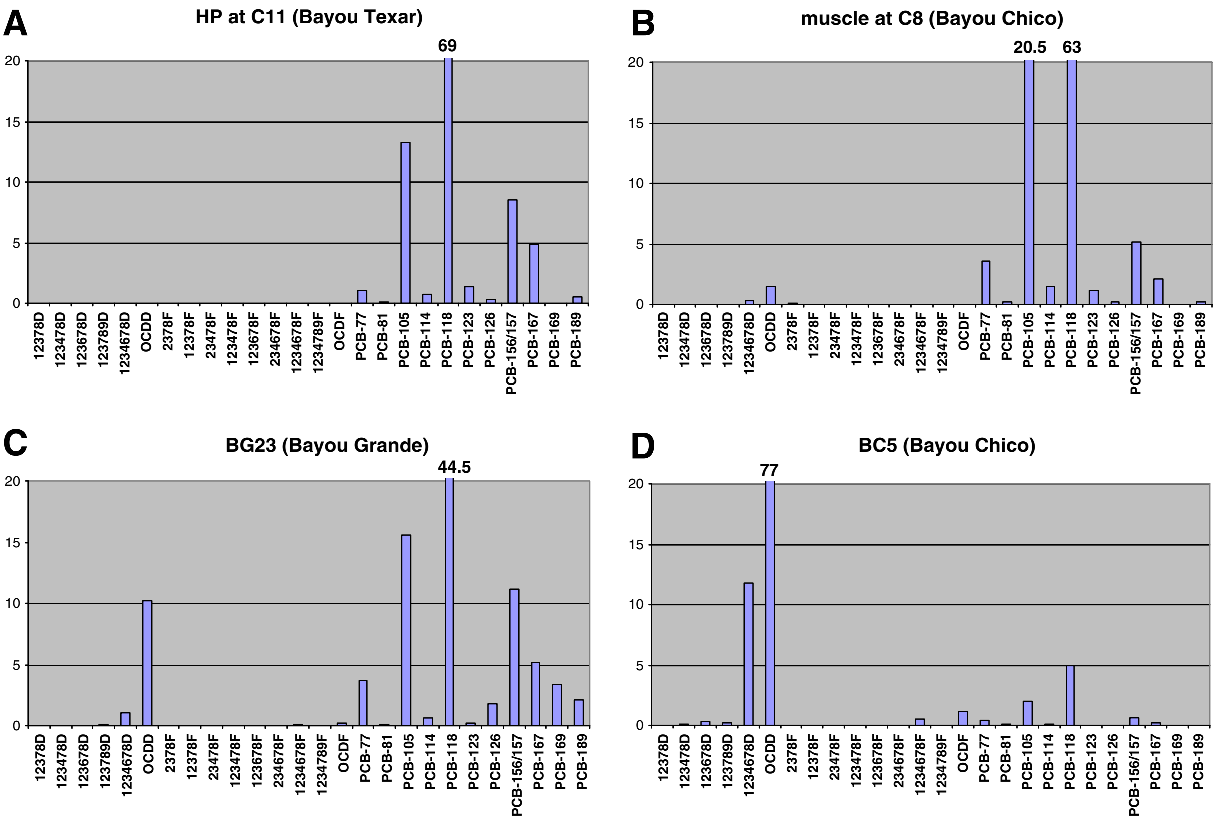

Fig. 9 PCDD/F and DL-PCB congener profiles as % of total combined mass concentration for samples from various parts of the factor loadings plot

Several authors have previously reported higher accumulation efficiencies for DL-PCBs in marine species (Bright et al. 1995; Lundebye et al. 2004; Micheletti et al. 2007). It has been argued that PCDD/Fs that are taken up are rapidly metabolized (Micheletti et al. 2007), although this has been demonstrated more clearly for fish than for blue crab (Gobas 1990). In fish, the bioconcentration factors of PCDDs and OCDF were approximately two orders of magnitude lower than those of PCBs of similar K_{ow} (Gobas 1990). The low bioconcentration and dietary bioaccumulation factors of the PCDDs were thought to be due to rapid depuration of the chemicals from the fish. Metabolic transformation of the PCDDs in the fish was shown to be an important factor causing this rapid depuration (Gobas 1990). In contrast, it has been argued that for DL-PCBs metabolism plays a smaller role and that in crabs and other estuarine species DL-PCB concentrations appear to be mainly regulated by their K_{ow} (Micheletti et al. 2007). Consequently, DL-PCBs accumulate faster than they are eliminated, and thus biomagnify in higher level consumers such as crabs (Bodin et al. 2007).

4 Conclusions

In general, mass concentrations of PCDD/Fs and DL-PCBs observed in sediments in the present study are comparable to those in other industrialized areas. The concentrations are higher in the sediments of Bayou Chico than in the other two estuaries, most likely due to the long history of industrial activities on the shores of Bayou Chico.

The total combined PCDD/F and DL-PCB TEQ in crab HP is generally higher than in sediments, but the TEQ concentration factor, expressed as the ratio of the total combined TEQ in crab HP and sediments, is inversely proportional to the total combined TEQ in the sediments. This shows that the augmentation of total combined TEQ in crab HP is limited and that

TEQ in crab HP does not continue to increase with increasing TEQ in sediment. This relationship is well pronounced in our dataset, in spite of the multiple processes and various trophic levels involved in bioaccumulation of sediment PCDD/Fs and DL-PCBs in blue crab. These findings are important for TEQ monitoring efforts because sediment TEQ is sometimes used as a proxy for biota TEQ.

The crabs have congener profiles that are systematically different from those in the sediments. The difference is more pronounced for PCDD/Fs than for the DL-PCBs, although DL-PCB accumulation by the crabs relative to the concentrations in the sediments is greater than that of PCDD/Fs. Compared to sediment profiles, more lesser-chlorinated PCDD/Fs that have higher TEFs, such as 12378 PeCDD (TEF=1.0) and 23478 PeCDF (TEF=0.3), accumulate in crab HP. This selective bioaccumulation of PCDD/Fs results in the TEQ augmentation in crab HP compared with sediments. Additionally, PCA shows that relative to sediment profiles more DL-PCBs than PCDD/Fs accumulate in crab HP and muscle. It also shows that the congener profiles in the crab samples are distinct from those in the sediments, regardless of the specific congener composition of the sediments. These observations indicate that the processes involved in bioaccumulation in blue crab are also selective for PCDD/Fs versus DL-PCBs.

Acknowledgments This study was supported by US EPA Cooperative Agreement award X-9745502 and grant no. R04/CCR421909 from the U.S. Centers for Disease Control and Prevention (CDC) to the Center for Environmental Diagnostics and Bioremediation at The University of West Florida. The contents of this article are solely the responsibility of the authors. Kristal Flanders managed the spatial databases for the project and drafted the maps. Alan Knowles, Jason Moore, Jeff Seebach, Tony DiGirolamo, Michael McAllister, Joseph Moss, Benjamin Finkes, Laura Penington, Anaduiska Rondon, Chris Carlton-Franco, Brandon Jarvis, Guy Allard, Danielle Peterson, Gustav Cancro, Brian Bradley, and Nicholas Balderston helped with the fieldwork and some laboratory procedures. The original manuscript benefited greatly from the comments by two anonymous reviewers.

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