

Accumulation of organic and inorganic contaminants in shellfish collected in estuarine waters near Pensacola, Florida: Contamination profiles and risks to human consumers

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Elevated levels of dioxins/furans and dioxin-like PCBs were detected in blue crabs and oysters from select locations in the Pensacola Bay region.

Abstract

We conducted a screening level assessment of contaminants in blue crabs (*Callinectes sapidus*) and oysters (*Crassostrea virginica*) from bays and bayous in the Pensacola, FL area. Tissue samples were analyzed for 17 dioxins/furans, 12 dioxin-like PCB (DL-PCBs) congeners, mercury, and various metals. Contaminant levels were compared to screening values (SV) calculated using U.S. EPA recommendations for establishing consumption advisories. All sampling locations exceeded the SV (0.098 pg g^{-1}) for dioxins/furans/DL-PCBs, based on a Florida-specific consumption rate (46 g day^{-1}). Arsenic (inorganic), mercury, cadmium, and zinc levels exceeded SVs in samples from select locations, and with the exception of mercury, these locations were generally downstream of known contaminated areas. We also assessed potential human health risks from consumption of these species. Risks to human health were greatest from consumption of crab hepatopancreas, suggesting that consumption of hepatopancreas, whether directly or indirectly, from crabs collected anywhere in the Pensacola Bay region should be avoided. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

The U.S. Environmental Protection Agency (U.S. EPA) reported that, for 2002, 32.9% of the nation's lake acreage, 15.3% of the total river miles, 100% of the Great Lakes and their connecting water bodies, and 71% of coastal waters, including 100% of the Gulf Coast were under fish consumption advisories (U.S. EPA, 2003). Although 39 chemicals were responsible for the advisories, mercury, PCBs, chlordane,

dioxins, and DDT accounted for the majority (96%) of consumption restrictions. These chemicals accumulate in the tissues of aquatic organisms at concentrations many times higher than concentrations in water, and may be biomagnified in the food chain to levels that cause physiological impairment at higher trophic levels and in human consumers. Although a number of these chemicals are no longer used or manufactured in the United States, studies have shown that they continue to accumulate in a variety of foods, including shellfish (Jensen and Bolger, 2001). For example, over 90% of human exposure to organochlorine compounds occurs through diet, primarily through seafood and meat (Smith and Gangolli, 2002). Segments of the human population with increased exposure risk include consumers of commercially harvested seafood, recreational and subsistence fishers.

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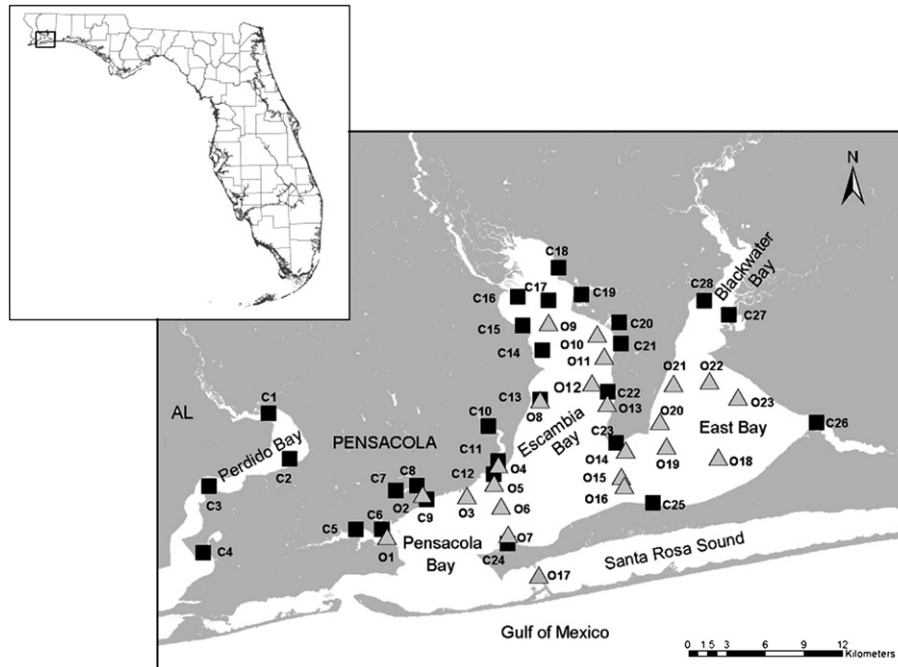


Fig. 1. Pensacola Bay area blue crab and oyster sampling locations. ■ = crab sampling station, ▲ = oyster sampling station.

The Pensacola Bay region is located at the western tip of the Florida Panhandle near the Florida-Alabama border (Fig. 1). Although historically the area supported a rich and diverse ecology and productive fisheries, many decades of point and non-point source pollution, habitat destruction, industrial activities, and development have impaired the health and productivity of the estuarine waters in the region (Thorpe et al., 1997). The area includes a number of historical and potential contaminant sources including paper mills, a coal-burning power plant, industrial complexes, military facilities, multiple Superfund sites, sewage outfalls, storm water discharges, atmospheric deposition, septic tanks, golf courses, and agriculture in the watershed. Although significant quantities of fish and shellfish are harvested and consumed in Northwest Florida, an extensive assessment of contaminant levels in fish and shellfish in the Pensacola Bay area has not been previously reported.

Commercial and recreational harvesting of fish and shellfish along the Gulf Coast and within the Pensacola Bay System is extensive and thus any potential contamination may present a toxicological risk to human consumers. Available information on contaminant body burdens in shellfish within the Pensacola Bay system exists as scattered and sporadic reports (Ache et al., 2000; Clark et al., 1986; Lewis et al., 2004; Oliver et al., 2001; Weis and Weis, 1992). These reports suggest a problem may exist for some shellfish species and in some areas of the ecosystem. In the present study, we report the results of a screening survey of contaminants in eastern oysters (*Crassostrea virginica*) and blue crabs (*Callinectes sapidus*) collected at multiple sites in the Pensacola Bay area. The objectives of this study were to determine whether these shellfish carry significant body burdens of toxic chemicals, identify chemical sources of concern exceeding screening values, and identify “hotspot” locations

of concern where elevated levels of contamination are found. Following the model established by the U.S. EPA in 2000, we analyzed the oyster and crab tissues for polychlorinated dibenzo-*p*-dioxins (PCDD)/dibenzofurans (PCDF), dioxin-like polychlorinated biphenyl (DL-PCB) congeners, and metals in order to define any public health risks and to provide a sensitive integrated indicator of regional contamination. To our knowledge, this is the first combined analyses of the 17 dioxins/furans and the 12 dioxin-like PCBs in blue crabs and oysters from various components of a bay system.

2. Methods

2.1. Sample collection

The Pensacola Bay watershed drains 18,100 km² of Florida and southern Alabama, and is comprised of five major estuaries – Pensacola, Escambia, Blackwater and East Bays, and Santa Rosa Sound (Thorpe et al., 1997). The estuaries receive drainage from four major rivers and many smaller tributaries and bayous. Perdido Bay is a small estuarine system that is fed by freshwater from the Perdido River and several smaller tributaries, and has a drainage area of 3100 km² (U.S. EPA, 1999). Samples were collected throughout the various estuaries and bayous draining into Pensacola Bay and on the Florida (east) side of Perdido Bay (Fig. 1). Most locations were identified by biologists and local crabbers/oystermen as areas of concern or significant harvest. Based on the EPA guidance for a screening study, we analyzed one composite sample for each target organism at each location.

Oysters (*C. virginica*) were collected from 23 locations between March 2003 and July 2004 by using tongs or by diving. Sampling locations were classified into three groups – bridges that span the major bays (O5–7, O9, and O14–17), commercial oyster beds (O10–13 and O18–23), and urbanized waterbodies (O1–4). Oysters were not collected from Perdido Bay because harvestable populations could not be identified. Upon collection, the samples were placed on wet ice for transport to the laboratory. Oyster shell length was measured and tissues were prepared by severing the adductor muscle, prying open the shell, and removing the soft tissue. A minimum of 10 oysters was

composited for each location and shipped to the analytical facilities for homogenization and analyses.

Blue crabs (*C. sapidus*) were collected between June 2003 and June 2004 from 28 locations, using 10 to 15 baited commercial crab traps deployed for 24–72 h at each location. Sampling locations were grouped as follows: Perdido Bay (C1–4), urbanized bayous (C5–12 and C24), western Escambia Bay (C13–17), eastern Escambia Bay (C18–22), and East/Blackwater Bay (C23 and C25–28). Crabs over 10.2 cm in carapace width were selected. Male crab migration ranges within an estuary are generally smaller than those of females (Ju and Harvey, 2002) and therefore, where possible, females were excluded from the analyses. Crabs were transported to the laboratory on wet ice. Tissues from seven to 15 crabs were composited for each location. Crab muscle and hepatopancreas were analyzed separately. Crabs were prepared by separating the carapace from the body and removing the hepatopancreas using forceps. All other internal organs were removed and discarded. Muscle tissue, was extracted by processing through a pre-cleaned compression device (Crab Master™). Claw meat was extracted using forceps. The tissues were homogenized using a stainless steel hand-held homogenizer and shipped to the analytical facilities for further homogenization and analyses.

2.2. Contaminant analysis

All tissue samples were analyzed for 17 dioxins/furans, 12 DL-PCB congeners (PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, and PCB-189), mercury, arsenic (total), cadmium, chromium, copper, lead, nickel, selenium, tin, and zinc. The majority of oyster samples was analyzed for organic contaminants by Triangle Laboratories, Inc. (Durham, NC). Crab samples and four oyster samples were analyzed by Alta Analytical Perspectives (Wilmington, NC). Dioxins/furans and PCBs in all samples were analyzed by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC-HRMS) using U.S. EPA methods 1668A and 8290B, respectively. Metals analyses were performed by the Florida Department of Health, Bureau of Laboratory Services (Jacksonville, FL) using Inductively Coupled Plasma – Mass Spectrometry (ICPMS; EPA method SW 846-6020) and cold vapor atomic absorption (CVAA; EPA method 245.6). Quality assurance/quality control (QA/QC) measures included analysis of method blanks, duplicate samples, matrix spikes, and laboratory control samples or standard reference materials (SRM). Average SRM (DOLT-2, DORM-2, or TORT-2) recovery efficiencies for metals ranged from 85–95%. Recoveries of 13C-labeled extraction standards ranged from 40% to 105% for dioxins and 25% to 113% for PCBs. Reported concentrations for PCBs and dioxins/furans were corrected for the recoveries of internal standards.

Wet weight concentrations are reported. A conversion factor of 15% was used to compare concentrations in oysters to dry-weight values reported in the literature (Ache et al., 2000; Lewis et al., 2004). Congeners below the detection limit were analyzed as one-half the detection limit ($ND = DL/2$). The detection limits of individual congeners varied depending on the sample masses, response factors and interferences. Detection limits for individual congeners averaged 0.03 to 0.25 pg g^{-1} for dioxins/furans and 0.03 to 0.15 pg g^{-1} for PCBs, on a wet-weight basis. For metals, detection limits were 0.70, 0.28, 0.62, 0.16, 0.30, 0.080, 0.45, 0.42, 0.10, and 0.02 mg kg^{-1} for Pb, Cr, Cu, Cd, Zn, As, Se, Ni, Sn, and Hg, respectively. If a chemical was not detected in any sample for a given target species, it was assumed absent and excluded from the analyses. Duplicate samples from a specific location were averaged to obtain one concentration.

2.3. Assessment of tissue contaminant levels

We calculated screening values (SV) as described by the U.S. EPA using a fish consumption rate estimate for Florida consumers of 46 g day^{-1} (Degner et al., 1994; U.S. EPA, 2000). The SVs are concentrations of chemicals in fish and shellfish tissue that are of potential public health concern and that are used as threshold values against which tissue levels of the contaminants can be compared (U.S. EPA, 2000). Screening values are calculated based on fish consumption rate (CR), mean body weight, for carcinogens – the Cancer Slope Factor (CSF; an upper bound risk estimate) and Risk Level (RL; maximum acceptable lifetime risk), and for non-carcinogens – the oral reference

dose (RfD; estimate of a daily exposure that is likely to be without appreciable risk of deleterious effects during a lifetime). A 70 kg body weight for adults, a 10^{-5} risk level for carcinogens, and a 70-year exposure duration were used in the calculations (U.S. EPA, 2000). CSFs and RfDs were obtained from the U.S. EPA (U.S. EPA, 2000, 2002).

We assessed the hazards posed by dioxins/furans and DL-PCBs using World Health Organization Toxic Equivalency Factors (TEFs) (Van den Berg et al., 1998) Toxic Equivalency Factors (TEFs) are weighing factors that compare the toxicity of a dioxin, furan or dioxin-like PCB congener to 2,3,7,8-TCDD, the most toxic dioxin congener. In a mixture, the TEFs of individual components are multiplied by their concentrations and the products are summed to give the Toxic Equivalency Quotient (TEQ). For development of fish consumption advisories, the TEQs are compared against the derived SVs. In the present report, we use TEQ_{DFP} to refer to TEQs calculated using both dioxins/furans and DL-PCBs, TEQ_{DF} to refer to TEQs calculated for dioxins/furans only, and TEQ_P to refer to TEQs calculated for DL-PCBs only. The TEQ_{DFP} SV used in the assessment was 0.098 pg g^{-1} .

To estimate the risk from consumption of all edible crab tissues (body muscle, claw, and hepatopancreas) we calculated contaminant concentrations for the whole crab using an estimate of 15% of total edible mass for hepatopancreas and 85% for muscle/claw (NJDEP, 2002; Tsai et al., 1984). Therefore, estimates for whole crab were calculated as follows: $(C_{\text{hep}} * 0.15) + (C_{\text{mus}} * 0.85)$, where C_{hep} = concentration in hepatopancreas and C_{mus} = concentration in crab muscle.

2.4. Risk calculations

We determined species-specific cancer and non-cancer hazard risks for each contaminant at each location to better estimate the human health risk from consumption of these shellfish (U.S. EPA, 2002). The potential cancer risk is an incremental increase in the probability of an individual developing cancer over a lifetime (U.S. EPA, 2002). The excess cancer risk for all carcinogens was summed to estimate total risk. Consumption rate and body weight were as described above. Exposure duration was varied to account for the effects of residence time on consumption risks and included nine years (median duration individuals remain at one residence), 30 years (national 90th percentile for duration at one residence), and 70 years (lifetime exposure duration) for adults (U.S. EPA, 2000, 2002). Likewise, we determined species-specific non-cancer hazard risks for each contaminant at each location. In these analyses, an exposure threshold was assumed to exist below which adverse effects were unlikely to occur, and thus the average daily dose was compared to the RfD to obtain a hazard quotient (HQ). A total Hazard Index (HI) was calculated by summing all HQ for a particular location across all health effects. If the total HI was greater than 1, HQs for chemicals with similar target organs or mechanisms of toxicity were summed to identify potential non-cancer effects (U.S. EPA, 2002).

2.5. Statistical analysis

Dioxin/furan and DL-PCB congener pattern profiles were analyzed by principal components analysis (PCA) using SPSS for Windows (Version 12.0, SPSS, Inc.). Individual congener concentrations were analyzed as TEQs to permit combined analysis of dioxins/furans and DL-PCBs. Therefore, each sample concentration was normalized to the WHO toxicity equivalent of 2,3,7,8-TCDD. Congener concentrations below the detection limit were assumed equal to one-half the detection limit. Congeners that were not detected in >90% of the samples were omitted from the analyses. A Varimax rotation was applied to the principal components (PC) for which eigenvalues exceeded 1.0. Factor scores for the first three PCs were plotted in three-dimensional space.

3. Results

3.1. Organic contaminants

Table 1 presents TEQ_{DFP} for the analyzed samples. Contaminant levels in all tissue types varied by study site (Tables 2–4).

Table 1
Toxic Equivalency Quotients (TEQ) for crab and oyster samples from the Pensacola Bay area

ID	Location/region	Crab muscle TEQ _{DFP} (pg g ⁻¹)	Hepatopancreas TEQ _{DFP} (pg g ⁻¹)	Total edible tissue TEQ _{DFP} (pg g ⁻¹)	ID	Location/sample type	Oysters TEQ _{DFP} (pg g ⁻¹)
C1	Perdido-11 Mile Creek	0.27	8.1	1.44	O1	Bayou Grande	4.21
C2	Perdido Bay – Upper	0.27	8.7	1.54	O2	Bayou Chico Bridge	5.90
C3	Perdido Bay – Lillian Bridge	0.11	12.3	1.94	O3	Bayfront Auditorium	1.86
C4	Perdido Bay – Tarkiln Bayou	0.17	7.2	1.23	O4	Bayou Texar	1.35
C5	Bayou Grande Upper	0.65	16.6	3.05	O5	Pensacola Bay Bridge North	1.54
C6	Bayou Grande	0.58	28.2	4.73	O6	Pensacola Bay Bridge Mid	0.43
C7	Bayou Chico Upper	0.84	38.6	6.50	O7	Pensacola Bay Bridge South	0.73
C8	Bayou Chico Bridge	0.87	30.5	5.32	O8	Gaberonne	1.42
C9	Bayou Chico Mouth	0.31	17.8	2.94	O9	I-10 Bridge Mid	1.82
C10	Bayou Texar Upper	0.60	13.4	2.52	O10	Escambia Bay 7	0.58
C11	Bayou Texar Mid	0.33	25.3	4.08	O11	Escambia Bay 1	0.46
C12	Bayou Texar Mouth	0.23	17.0	2.75	O12	Escambia Bay 5	0.62
C13	Gaberonne	0.87	32.8	5.65	O13	Escambia Bay 8	0.56
C14	Devils Point	0.34	16.3	2.74	O14	Garcon Point Bridge North	1.14
C15	Escambia Bay NW	0.75	14.4	2.80	O15	Garcon Point Bridge Mid	0.90
C16	Mackey Cove	0.38	9.3	1.72	O16	Garcon Point Bridge South	0.93
C17	Escambia Channel	0.76	18.7	3.45	O17	Bob Sikes Bridge Mid	1.19
C18	Escambia Bay NE	0.28	14.5	2.41	O18	East Bay 13	0.37
C19	Mulat Bayou	0.44	8.1	1.58	O19	East Bay 2	0.31
C20	Indian Bayou	0.46	14.8	2.61	O20	East Bay 3	0.29
C21	Trout Bayou	0.46	20.8	3.51	O21	East Bay 5	0.33
C22	Escambia Bay SE	0.67	14.7	2.76	O22	East Bay 8	0.29
C23	Garcon Point	0.13	3.1	0.58	O23	East Bay 9	1.14
C24	Hoffman Bayou	0.32	12.4	2.13			
C25	Redfish Point	0.26	17.4	2.82			
C26	East River	0.33	9.7	1.73			
C27	Yellow River	0.54	3.3	0.96			
C28	Blackwater Bay	0.33	4.1	0.90			

ID designations correspond to locations on Fig. 1. TEQ_{DFP} were calculated using TEF values derived by the WHO and by substituting one-half the detection limit (ND = DL/2) for dioxin, furan or PCB congeners that were below the detection limit.

In general, the highest TEQ_{DFP} in crab muscle, crab hepatopancreas, and total edible crab tissue were observed in samples from western Escambia Bay (C13, C15, C17) and from the urbanized bayous (C6, C7, C8). Likewise, in oysters, the lowest TEQ_{DFP} were observed for oyster samples from the commercial oyster beds in East Bay (O18–22) and Escambia Bay (O11–13), and the highest TEQ_{DFP}s were found in samples taken from the urbanized waterbodies (O1–3). All of the sampling locations exceeded the calculated SV (0.098 pg g⁻¹) for dioxins/furans/DL-PCBs. The two most toxic dioxin congeners, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, were detected in 100% of the hepatopancreas samples although they represented only a fraction of the total dioxins/furans. OCDD and 1,2,3,4,6,7,8-HpCDD were the most prevalent congeners in most samples. All DL-PCB congeners were detected in all crab samples, although PCB-169 and PCB-189 were not recovered from many oyster samples. PCB-118 was the most prevalent congener in all samples, followed by PCB-156.

3.2. Congener fingerprint analysis

The contribution of DL-PCBs and dioxins/furans to TEQ_{DFP} varied extensively by sampling location. Principal components analysis was used to characterize the distribution of congeners in the samples. The model described 88.2% of the variance over four PCs with eigenvalues over 1 for hepatopancreas.

The samples formed five distinct clusters (Fig. 2). Cluster A included samples from Perdido Bay and Blackwater/East Bays, which had the lowest levels of both dioxins/furans and DL-PCBs, as demonstrated by their low TEQ_{DFP} values. Samples from Western Escambia Bay and Bayou Grande formed Cluster B. These sites are located downstream of known PCB sources – in Escambia Bay, a chronic industrial release (3.8–11.4 L/day) of PCBs in the late 1960's, and in Bayou Grande, a PCB-containing Superfund site at Naval Air Station Pensacola (NASP) (Parrar et al., 1969; Tetra Tech NUS, 2003). Cluster C is composed of samples from eastern Escambia Bay. Cluster D contains two samples from Bayou Chico, a historically industrialized bayou known to contain high sediment levels of multiple chemicals, including PCBs and dioxins (Debusk et al., 2002). Cluster E included samples from throughout the sampling area, including several urban bayous. Four samples remained separate from any of the major clusters. Sample C13 (Gaberonne), which projected apart from all other locations, was located in western Escambia Bay and exhibited the highest levels of DL-PCBs. In general, samples with higher levels of DL-PCBs projected further from the origin, along PC2.

Crab muscle samples exhibited a similar, but not as clearly defined cluster pattern as hepatopancreas (Fig. 3). The model accounted for 89.3% of the variability across the five PCs with eigenvalues over 1.0. Cluster A contained the samples that corresponded to Cluster A in the hepatopancreas model – those

Table 2
Dioxin/furan (pg g⁻¹), dioxin-like PCB (pg g⁻¹), and metals concentrations (mg kg⁻¹) in crab hepatopancreas samples

Analyte	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
2378-TCDD	0.6	1.0	0.7	0.7	0.3	0.3	3.5	2.6	1.3	0.5	0.8	0.6	0.8
12378-PeCDD	1.5	1.1	2.2	2.2	1.2	1.2	7.6	4.5	3.4	1.4	3.3	2.0	2.4
123478-HxCDD	0.9	0.4	0.6	0.5	0.6	0.6	5.1	3.0	2.0	0.5	1.9	1.2	1.7
123678-HxCDD	1.9	0.9	3.1	1.7	1.5	1.4	23.1	11.1	7.5	1.4	5.8	3.5	4.8
123789-HxCDD	2.0	0.4	1.1	0.7	1.0	0.8	9.5	5.4	3.3	0.7	3.1	2.8	3.6
1234678-HpCDD	4.3	1.2	3.2	1.8	3.0	2.4	61.4	54.7	13.3	2.2	8.4	6.4	5.7
OCDD	5.2	3.5	5.7	3.1	6.0	5.2	106.0	121.0	12.7	5.7	9.1	9.1	11.7
2378-TCDF	2.0	3.6	2.4	2.2	3.7	4.1	22.2	35.5	7.0	3.0	7.9	5.5	10.2
12378-PeCDF	2.0	2.2	2.6	1.6	5.2	0.7	5.6	7.0	1.6	3.2	1.1	0.6	0.9
23478-PeCDF	1.2	1.2	1.7	1.3	2.2	2.3	5.0	4.0	2.7	1.6	4.3	2.0	3.1
123478-HxCDF	0.4	0.5	1.6	0.1	1.1	0.3	2.7	1.8	1.1	0.5	0.8	0.3	0.3
123678-HxCDF	3.6	5.5	24.7	7.3	22.2	0.3	1.7	4.8	0.8	3.8	0.9	0.4	0.4
123789-HxCDF	0.1	0.1	0.1	0.1	0.2	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0
234678-HxCDF	0.2	0.1	0.1	0.1	0.1	0.3	1.0	0.5	0.4	0.1	0.7	0.3	0.3
1234678-HpCDF	15.3	15.3	76.4	25.1	55.1	0.4	6.3	10.0	2.6	6.8	2.2	0.5	0.5
1234789-HpCDF	0.8	0.2	0.2	0.1	0.4	0.0	0.0	0.1	0.0	0.6	0.0	0.0	0.0
OCDF	0.1	0.0	0.5	0.2	0.2	0.1	0.9	1.0	0.1	0.1	0.3	0.1	0.0
TEQ _{DF}	4.2	5.2	8.0	4.0	6.5	3.4	21.1	162	8.5	4.0	8.5	5.1	7.0
PCB-77	79.7	102.0	104.0	120.0	136.0	224.0	1310.0	1130.0	578.0	256.0	630.0	364.0	587.0
PCB-81	4.7	5.4	5.6	5.6	14.0	27.1	90.3	65.9	28.6	15.0	29.9	16.0	25.4
PCB-105	1065	1330	1770	1340	2250	3070	9020	8350	4310	3090	5610	4900	8190
PCB-114	57.8	63.2	87.3	56.2	138.0	162.0	615.0	586.0	248.0	169.0	290.0	239.0	1020.0
PCB-118	4775	7410	7350	6330	12,000	13,500	29,400	26,700	15,600	16,000	27,100	22,000	64,700
PCB-123	96.2	122.0	141.0	122.0	226.0	232.0	558.0	562.0	233.0	326.0	451.0	407.0	953.0
PCB-126	22.7	24.8	26.1	23.0	73.4	213.0	115.0	86.3	58.8	63.0	117.0	68.8	114.0
PCB-156/157	729	973	1297	797	2141	3160	2880	3163	2040	1986	2840	3560	12,600
PCB-167	417	570	533	476	1650	2460	1310	1360	932	1130	1520	1660	5570
PCB-169	3.4	2.3	3.3	2.2	19.5	4.9	18.3	5.8	23.6	4.8	20.7	29.5	6.1
PCB-189	64.3	104.0	121.0	63.5	270.0	459.0	144.0	174.0	121.0	125.0	96.4	194.0	414.0
TEQ _P	3.9	3.6	4.3	3.3	10.2	24.8	17.5	14.3	9.4	9.4	16.9	11.9	25.8
As	3.00	2.40	2.60	8.15	2.00	3.80	2.50	5.00	9.60	2.30	2.30	3.30	3.30
In. As	0.060	0.048	0.052	0.163	0.040	0.076	0.050	0.100	0.192	0.046	0.046	0.066	0.066
Cd	0.14	0.01	0.19	0.20	0.98	4.60	0.24	0.67	2.30	4.00	0.65	1.30	1.90
Cr	0.55	1.10	1.10	0.92	0.60	0.29	0.11	0.64	0.32	0.44	0.30	0.32	0.50
Cu	6.10	7.20	5.20	7.60	28.00	58.00	95.00	52.00	99.00	88.00	40.00	32.00	53.00
Pb	0.31	0.25	0.31	0.32	0.15	0.30	0.29	0.36	0.27	0.33	0.28	0.15	0.36
Hg	0.05	0.02	0.22	0.13	0.14	0.06	0.02	0.05	0.06	0.08	0.05	0.10	1.10
Ni	0.19	0.15	0.19	0.56	0.09	0.18	0.18	0.22	0.17	0.20	0.17	0.21	0.22
Se	2.00	1.80	1.90	1.85	1.60	1.60	0.98	1.30	1.30	1.80	1.10	1.10	1.20
Sn	0.44	0.35	0.45	0.46	0.75	0.04	0.04	0.50	0.04	0.47	0.04	0.02	0.05
Zn	17.0	18.0	17.0	21.5	19.0	46.0	46.0	43.0	48.0	14.0	34.0	48.0	45.0

Numbers in bold represent samples for which concentrations were below the detection limit (DL), and the concentration is expressed as DL/2. Locations correspond with those indicated on Fig. 1.

that exhibited the lowest total levels of contamination. Likewise, Cluster C of the crab muscle model corresponded to Cluster D of the hepatopancreas model. Samples with the highest levels of DL-PCBs, specifically PCB-118, PCB-123, and PCB-156/157, projected farthest from the origin along PC2 and thus, Cluster B contained two samples from western Escambia Bay.

PCA of oyster samples resulted in a model that accounted for 90.4% of the variance over three PCs with eigenvalues over 1.0. The samples formed two major clusters (Fig. 4). Cluster A included all of the commercial oyster bed samples and a number of samples from bridge pilings. These samples exhibited the lowest dioxin and PCB levels. Cluster B contained a mixture of samples from throughout the sampling area, including two bridge samples, a sample from an urban bayou, and from the commercial port area along the city of

Pensacola waterfront. The remaining four samples were not similar to any of the clusters. Sample O2 (Bayou Chico), projected to the same location as its corresponding crab muscle and hepatopancreas samples and had the highest TEQ_{DFP} of all samples as a result of the highest dioxin levels and the second-highest DL-PCB levels. Sample O1 (Bayou Grande) projected farthest from the origin along PC2 and exhibited the highest PCB levels of all samples. DL-PCBs in this sample, collected downstream of the NASP Superfund site, accounted for 80% of the TEQ_{DFP}.

3.3. Inorganic contaminants

Tables 2–4 present metal concentrations in the analyzed tissues. None of the samples exceeded detection limits for lead, and cadmium levels were below detection limits in

C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28
0.6	0.3	0.4	0.6	0.4	0.2	0.2	0.6	0.6	0.1	0.4	0.9	0.5	0.3	0.4
0.9	0.7	0.4	0.9	0.9	0.6	1.2	3.9	1.2	0.6	2.2	4.7	1.8	0.8	0.9
0.5	0.5	0.3	0.5	0.4	0.3	0.8	1.8	0.5	0.4	1.1	2.2	1.3	0.3	0.4
1.2	1.3	0.7	1.4	0.9	0.9	2.4	6.9	1.1	0.8	3.6	10.0	3.3	0.7	0.7
1.2	1.0	0.7	1.1	0.7	0.7	1.7	2.8	0.9	0.7	1.4	4.6	2.7	0.9	0.8
3.9	4.4	2.9	2.0	2.0	2.3	4.0	10.6	2.2	1.5	5.2	13.4	7.6	1.5	1.5
20.6	17.8	21.9	10.7	9.1	7.8	7.1	16.1	9.6	4.3	8.9	14.4	11.2	4.7	4.8
4.3	3.1	2.7	2.6	2.8	1.9	3.1	4.7	3.5	1.0	2.9	4.5	2.9	0.8	1.0
1.3	0.9	0.5	2.5	2.7	1.5	5.6	3.5	4.6	0.4	1.1	3.2	1.8	0.3	0.4
0.3	0.8	0.1	1.0	1.0	0.6	1.7	1.9	1.3	0.3	1.4	2.5	1.6	0.4	0.5
0.4	0.3	0.2	0.1	0.1	0.1	0.1	0.9	0.6	0.1	0.5	0.9	0.5	0.1	0.2
3.2	2.3	1.0	11.9	10.4	1.6	5.3	8.0	11.4	0.5	2.3	8.6	6.2	0.1	0.9
0.0	0.7	0.0	0.1	0.1	0.3	0.2	3.3	0.1	0.0	0.1	0.1	0.1	0.1	0.1
0.1	0.6	0.1	0.2	0.1	0.2	0.1	3.1	0.1	0.0	0.3	0.1	0.3	0.1	0.1
6.6	7.5	2.1	50.2	46.7	4.2	16.5	28.5	54.3	1.0	4.1	312	19.3	0.0	2.3
0.1	0.0	0.0	0.1	0.1	0.0	0.2	0.1	0.4	0.0	0.1	0.1	0.3	0.1	0.4
0.0	0.1	0.0	0.1	0.2	0.0	0.1	0.2	0.2	0.0	0.0	0.0	0.3	0.1	0.1
3.0	2.5	1.5	4.4	4.0	1.8	4.2	9.3	5.0	1.3	4.7	10.5	5.2	1.6	2.0
440.0	331.5	329.0	335.0	402.0	226.0	209.0	236.0	257.0	40.7	166.0	162.0	127.0	56.8	53.4
14.3	10.5	8.5	11.2	11.6	7.3	11.6	13.8	11.1	2.2	9.7	9.6	7.0	2.2	2.5
5480	5155	3570	4110	5870	2520	3820	4320	3545	626	3040	2300	1480	616	755
338.0	274.0	191.0	170.0	274.0	92.9	191.0	224.0	169.5	28.2	164.0	132.0	70.9	27.2	35.3
33,700	25,600	22,100	20,800	32,700	15,600	25,200	25,400	20,350	3000	13,633	11,800	8210	2560	3430
614.0	513.0	388.0	314.0	501.0	250.0	460.0	475.0	332.0	52.4	254.3	213.0	173.0	48.8	67.8
63.8	58.0	35.9	60.3	72.3	36.1	56.6	62.0	52.3	11.3	46.5	432	27.6	10.5	12.2
5390	5430	2852	3432	5840	1463	3632	4140	3626	605	2379	1992	1315	559	768
2390	2105	1310	1610	2590	1016	1980	2070	1800	271	1091	1040	718	262	349
3.4	2.7	1.4	4.4	4.4	1.5	3.6	5.0	3.7	1.2	5.7	5.8	3.1	1.5	1.6
310.0	258.5	122.0	192.0	320.0	64.9	196.0	214.0	189.0	47.8	185.0	125.0	78.3	38.5	42.2
13.4	11.9	7.8	14.3	10.5	6.3	10.6	11.5	9.7	1.8	7.7	6.9	4.5	1.7	2.1
1.90	1.75	1.80	1.60	2.40	1.50	2.05	2.10	4.00	2.90	3.40	4.20	4.40	1.70	2.10
0.038	0.035	0.036	0.032	0.048	0.030	0.041	0.042	0.080	0.058	0.068	0.084	0.088	0.034	0.042
0.67	1.80	0.89	0.66	0.63	1.40	0.91	1.20	0.64	1.60	0.90	0.95	0.51	1.10	0.82
0.55	0.76	0.38	0.28	0.14	0.58	0.34	0.77	0.20	0.39	0.76	0.65	0.60	0.31	0.51
56.00	76.00	64.00	41.00	22.00	20.00	10.95	11.00	32.00	46.00	68.00	42.00	7.00	26.00	22.00
0.32	0.32	0.30	0.34	0.35	0.33	0.33	0.33	0.31	0.35	0.33	0.35	0.24	0.36	0.39
0.25	0.07	0.06	0.05	0.04	0.52	0.06	0.08	0.04	0.08	0.05	0.07	0.13	0.06	0.04
0.19	0.34	0.18	1.40	0.21	0.20	0.47	0.20	1.30	0.55	0.20	0.21	0.15	0.22	1.3
2.30	1.75	1.80	1.20	1.50	1.10	1.65	1.30	1.60	1.50	1.27	2.00	2.10	1.50	1.70
0.46	0.46	0.43	0.48	0.50	0.47	0.27	0.47	0.44	0.50	0.47	1.1	0.35	0.50	0.55
19.0	26.0	21.0	37.0	33.0	13.0	22.0	18.0	43.0	16.0	33.7	28.0	16.0	20.0	32.0

all crab muscle samples. Only six hepatopancreas samples exceeded the SV for cadmium (1.52 mg kg⁻¹) and these samples were located primarily in the urbanized sampling locations. The majority of crab muscle and hepatopancreas nickel and tin concentrations fell below their respective detection limits. None of the samples that were above the nickel detection limits exceeded the calculated SV (30.4 mg kg⁻¹). None of the samples exceeded the SVs for chromium or selenium (4.56 and 7.61 mg kg⁻¹, respectively). Four oyster samples exceeded the SV for zinc (456.32 mg kg⁻¹). A SV could not be calculated for total tin or copper due to a lack of RfD or CSF values. The highest copper levels in both crab hepatopancreas and oysters were found in samples collected from the urban bayous and western Escambia Bay.

EPA consensus toxicity values are available only for inorganic arsenic and therefore, we estimated the levels of

inorganic arsenic by applying a conversion factor to the total arsenic levels measured in each sample. A separate analysis of three crab, three hepatopancreas, and three oyster samples from the Pensacola region revealed that inorganic arsenic levels were generally below 1% of total arsenic in crab muscle and oysters, and below 2% for crab hepatopancreas (unpublished data). Therefore, for screening purposes, we estimated the inorganic arsenic concentrations using 1% of total arsenic as a conversion factor for crab muscle and oysters and 2% for crab hepatopancreas. All of the hepatopancreas samples, 15 of 28 crab muscle samples, 26 of 28 estimated total edible crab tissue samples, and 22 of 23 oyster samples exceeded the SV for inorganic arsenic (0.010 mg kg⁻¹). The highest arsenic levels in crab muscle and hepatopancreas were observed at the mouth of Bayou Chico (C9), an industrialized bayou that historically and/or presently receives drainage from a number of

Table 3
Dioxin/furan (pg g⁻¹), dioxin-like PCB (pg g⁻¹), and metals concentrations (mg kg⁻¹) in crab muscle samples

Congener	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
2378-TCDD	0.03	0.03	0.01	0.03	0.03	0.02	0.10	0.13	0.03	0.04	0.02	0.02	0.05
12378-PeCDD	0.05	0.01	0.01	0.04	0.06	0.03	0.17	0.21	0.07	0.11	0.06	0.01	0.06
123478-HxCDD	0.02	0.23	0.01	0.29	0.02	0.02	0.09	0.15	0.06	0.03	0.01	0.02	0.01
123678-HxCDD	0.02	0.25	0.05	0.31	0.02	0.02	0.43	0.52	0.19	0.08	0.08	0.08	0.11
123789-HxCDD	0.02	0.28	0.01	0.33	0.06	0.02	0.22	0.25	0.10	0.07	0.05	0.03	0.10
1234678-HpCDD	0.13	0.02	0.10	0.07	0.24	0.08	1.95	3.64	0.65	0.19	0.19	0.03	0.02
OCDD	0.29	0.35	0.36	0.42	1.06	0.23	6.17	16.00	2.04	0.61	0.55	0.04	0.03
2378-TCDF	0.03	0.10	0.03	0.05	0.23	0.11	0.48	0.64	0.13	0.16	0.15	0.11	0.22
12378-PeCDF	0.04	0.09	0.03	0.06	0.19	0.01	0.16	0.21	0.04	0.10	0.02	0.02	0.04
23478-PeCDF	0.01	0.03	0.01	0.02	0.11	0.08	0.10	0.01	0.02	0.06	0.05	0.02	0.04
123478-HxCDF	0.02	0.05	0.01	0.02	0.02	0.03	0.08	0.10	0.05	0.04	0.03	0.03	0.00
123678-HxCDF	0.08	0.13	0.15	0.16	0.41	0.01	0.05	0.15	0.03	0.07	0.01	0.01	0.00
123789-HxCDF	0.02	0.07	0.02	0.03	0.03	0.01	0.01	0.04	0.01	0.04	0.01	0.01	0.01
234678-HxCDF	0.02	0.05	0.01	0.02	0.02	0.01	0.01	0.04	0.01	0.03	0.01	0.01	0.01
1234678-HpCDF	0.30	0.62	0.48	0.87	1.11	0.01	0.15	0.39	0.09	0.03	0.03	0.01	0.04
1234789-HpCDF	0.04	0.03	0.02	0.03	0.04	0.01	0.03	0.05	0.01	0.05	0.01	0.02	0.01
OCDF	0.05	0.05	0.17	0.15	0.31	0.03	0.11	0.04	0.08	0.03	0.07	0.05	0.04
TEQ _{DF}	0.18	0.21	0.06	0.11	0.25	0.12	0.49	0.58	0.18	0.24	0.13	0.06	0.18
PCB-105	22.6	36.8	20.7	26.8	91.8	45.3	197.0	230.0	65.1	104.0	80.0	70.3	145.0
PCB-77	1.59	3.89	1.83	3.3	7.59	4.25	36.30	40.00	10.50	8.36	11.22	4.84	14.90
PCB-81	0.10	0.14	0.08	0.12	0.64	0.60	1.97	2.23	0.45	0.56	0.47	0.32	0.69
PCB-114	1.17	1.48	0.86	1.02	5.09	2.51	10.30	16.00	3.64	7.02	3.68	1.70	7.77
PCB-118	94.3	165.0	75.8	110.0	426.0	225.0	509.0	704.0	220.0	659.0	344.5	299.0	897.0
PCB-123	1.67	2.39	1.35	1.87	7.24	3.75	9.21	12.90	3.66	11.6	5.60	4.75	13.80
PCB-126	0.39	0.60	0.31	0.43	3.03	3.99	1.86	2.18	0.82	2.36	1.31	1.07	2.52
PCB-156/157	12.2	18.9	9.9	11.0	65.0	41.0	36.3	57.0	23.3	75.1	33.7	25.5	115.0
PCB-167	6.18	10.70	4.60	6.21	51.5	34.00	14.60	23.40	10.00	42.3	16.15	17.70	53.70
PCB-169	0.02	0.02	0.07	0.01	0.81	1.18	0.27	0.13	0.29	0.2	0.39	0.29	26.95
PCB-189	0.76	1.63	0.63	0.66	6.02	3.44	1.32	1.88	0.84	2.9	1.19	0.22	0.22
TEQ _P	0.09	0.06	0.05	0.06	0.40	0.46	0.36	0.29	0.13	0.36	0.20	0.17	0.69
As	0.90	1.20	1.10	2.80	1.10	1.50	2.00	3.30	8.30	0.73	0.69	1.32	2.20
In. As	0.009	0.012	0.011	0.028	0.011	0.015	0.020	0.033	0.083	0.007	0.007	0.013	0.022
Cd	0.05	0.09	0.07	0.07	0.06	0.08	0.08	0.08	0.06	0.07	0.08	0.05	0.08
Cr	0.79	0.98	0.82	0.67	0.49	0.14	0.13	0.28	0.11	0.29	0.13	0.17	0.37
Cu	4.40	5.10	4.00	5.90	5.90	7.70	11.00	6.70	12.00	11.00	8.15	8.95	14.00
Pb	0.23	0.39	0.28	0.32	0.26	0.35	0.32	0.34	0.26	0.30	0.33	0.23	0.35
Hg	0.13	0.14	0.24	0.13	0.12	0.14	0.07	0.14	0.15	0.22	0.15	0.17	0.21
Ni	0.14	0.24	0.17	0.19	0.16	0.21	0.19	0.20	0.16	0.18	0.29	0.14	0.21
Se	0.90	1.00	1.00	1.00	0.84	0.60	0.53	0.67	0.73	0.81	0.51	0.50	0.57
Sn	0.32	0.55	0.39	0.46	0.37	0.05	0.05	0.48	0.04	0.43	0.05	0.03	0.05
Zn	22.0	25.0	24.0	28.0	20.0	29.0	40.0	29.0	43.0	26.0	34.5	34.0	54.0

Numbers in bold represent samples for which concentrations were below the detection limit (DL), and the concentration is expressed as DL/2. Locations correspond with those indicated on Fig. 1.

chemical, industrial, and wood treatment/processing facilities. In oysters, arsenic concentrations were similar throughout the sampling area with little variation between locations.

Mercury is assimilated by fish and shellfish primarily as methyl mercury (Faurey et al., 1997; U.S. EPA, 2000) and therefore, total mercury was used as a surrogate measurement for methyl mercury. Mercury levels were lowest in oysters and highest in crab muscle. None of the oyster samples exceeded the mercury SV (0.15 mg kg⁻¹). Sixteen crab muscle samples, four hepatopancreas samples, and 12 total edible crab tissue samples exceeded the SV. However, only one sample (hepatopancreas from C13) exceeded the State of Florida's "Do not eat" advisory level (0.85 mg kg⁻¹) for sensitive populations (women of childbearing age and children) and none of the samples exceeded the advisory level for the general public

(1.5 mg kg⁻¹). Likewise, only two samples exceeded the U.S. EPA SV of 0.4 mg kg⁻¹ that is based on a consumption rate of 17.5 g day⁻¹ (hepatopancreas from C19 and C13).

3.4. Risk characterization

While the EPA-based SV is a threshold above which fish consumption advisories may be required, the SV does not characterize the specific health hazards for individuals consuming the fish or shellfish. We therefore utilized risk assessment guidance developed by the EPA to estimate the potential for adverse health effects in consumers of blue crabs and oysters from the Pensacola Bay region. We analyzed the tissue samples for two contaminant groups that are classified as

C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28
0.02	0.03	0.03	0.03	0.02	0.01	0.02	0.02	0.04	0.02	0.03	0.02	0.03	0.02	0.02
0.13	0.09	0.07	0.04	0.04	0.07	0.06	0.11	0.29	0.02	0.05	0.03	0.05	0.23	0.16
0.04	0.05	0.04	0.04	0.04	0.02	0.04	0.05	0.43	0.04	0.03	0.02	0.06	0.31	0.13
0.04	0.11	0.03	0.03	0.04	0.06	0.09	0.18	0.41	0.04	0.15	0.11	0.12	0.31	0.12
0.05	0.10	0.04	0.04	0.04	0.04	0.07	0.13	0.46	0.05	0.07	0.06	0.12	0.34	0.15
0.06	0.55	0.15	0.22	0.09	0.29	0.24	0.51	0.06	0.25	0.39	0.26	0.34	0.09	0.07
0.49	3.07	1.30	2.15	0.84	1.55	0.75	1.73	0.47	1.19	1.23	0.79	0.94	0.70	0.73
0.02	0.21	0.09	0.20	0.04	0.11	0.12	0.12	0.06	0.04	0.08	0.10	0.10	0.03	0.03
0.04	0.08	0.06	0.03	0.02	0.15	0.11	0.07	0.05	0.02	0.05	0.11	0.06	0.14	0.05
0.04	0.02	0.06	0.03	0.02	0.04	0.03	0.03	0.06	0.02	0.06	0.05	0.07	0.14	0.05
0.02	0.02	0.02	0.03	0.03	0.02	0.03	0.04	0.04	0.04	0.02	0.02	0.08	0.09	0.10
0.02	0.11	0.02	0.27	0.13	0.08	0.18	0.10	0.10	0.01	0.03	0.19	0.11	0.08	0.09
0.03	0.04	0.03	0.04	0.03	0.03	0.03	0.05	0.05	0.01	0.03	0.02	0.05	0.13	0.13
0.02	0.03	0.02	0.03	0.03	0.02	0.02	0.04	0.04	0.01	0.03	0.02	0.04	0.10	0.10
0.05	0.49	0.05	1.72	0.79	0.36	0.67	0.38	0.61	0.02	0.13	0.91	0.53	0.04	0.05
0.06	0.02	0.06	0.02	0.04	0.03	0.03	0.02	0.05	0.03	0.03	0.05	0.04	0.05	0.07
0.05	0.31	0.06	0.04	0.20	0.04	0.16	0.14	0.06	0.06	0.03	0.04	0.20	0.06	0.05
0.20	0.21	0.16	0.18	0.12	0.14	0.16	0.23	0.52	0.07	0.16	0.14	0.19	0.47	0.29
70.8	259.5	128.0	290.0	77.2	120.0	118.5	97.7	72.1	22.5	77.3	42.3	51.3	23.5	15.4
6.56	20.80	18.60	36.60	6.74	10.60	7.93	6.84	7.64	2.05	4.46	4.68	5.52	2.48	1.19
0.19	0.59	0.32	0.74	0.18	0.37	0.40	0.36	0.21	0.11	0.27	0.30	0.01	0.1	0.07
3.31	12.95	4.55	12.00	2.82	4.72	5.27	4.52	2.36	1.08	3.66	2.14	2.11	1.13	0.75
331.0	1320.0	629.0	1410.0	333.0	851.0	758.5	558.0	314.5	104.0	307.3	192.0	259.0	106.0	60.7
5.24	23.10	9.19	21.40	4.80	12.30	12.45	9.7	4.90	1.83	4.97	3.41	5.05	1.8	1.06
0.68	2.67	1.11	3.10	0.88	1.66	1.63	1.29	0.86	0.39	0.95	0.80	0.85	0.44	0.23
39.6	210.9	58.3	180.6	44.8	61.0	82.0	69.0	42.8	11.8	40.3	28.9	35.4	18.3	9.4
15.70	81.95	25.00	81.60	19.90	46.20	48.45	35.5	20.30	6.54	17.17	14.20	19.40	7.91	4.04
0.02	0.18	0.05	0.15	0.07	0.01	0.11	0.11	0.08	0.06	0.09	0.02	0.02	0.07	0.04
1.36	7.08	1.52	4.92	1.78	1.69	2.63	2.42	1.44	0.43	1.77	1.44	1.61	0.9	0.41
0.13	0.54	0.22	0.58	0.16	0.30	0.30	0.23	0.15	0.06	0.16	0.12	0.14	0.07	0.04
0.57	0.84	0.54	0.50	0.69	0.55	0.47	0.56	1.75	3.70	2.07	2.50	2.40	0.55	0.70
0.006	0.008	0.005	0.005	0.007	0.006	0.005	0.006	0.018	0.037	0.021	0.025	0.024	0.006	0.007
0.09	0.08	0.08	0.08	0.07	0.07	0.07	0.06	0.07	0.07	0.07	0.06	0.07	0.09	0.07
0.40	0.42	0.14	0.14	0.13	0.52	0.12	0.36	0.12	0.13	0.49	0.72	0.52	0.17	0.26
7.80	9.90	4.20	8.40	11.00	6.40	6.10	8.10	9.65	3.90	4.33	7.60	7.50	4.40	9.30
0.38	0.32	0.34	0.34	0.32	0.31	0.29	0.23	0.30	0.31	0.31	0.25	0.32	0.41	0.30
0.14	0.19	0.15	0.19	0.13	0.08	0.17	0.23	0.13	0.23	0.15	0.16	0.11	0.15	0.21
0.23	0.41	0.20	0.87	0.60	0.19	0.18	0.30	0.47	0.19	0.18	0.15	0.19	0.25	0.18
0.66	0.68	0.51	0.58	0.51	0.65	0.49	0.58	0.29	0.59	0.47	1.00	1.10	0.68	0.84
0.55	0.45	0.48	0.50	0.46	0.44	0.04	0.33	0.42	0.45	0.44	0.77	0.45	0.60	0.42
32.0	36.5	24.0	36.0	33.0	35.0	26.5	25.0	29.0	14.0	22.0	20.0	27.0	24.0	28.0

carcinogens and for which a CSF is available – dioxins/furans/DL-PCBs and arsenic (inorganic). Crab hepatopancreas samples exceeded a cancer risk of 1×10^{-4} in all but three samples (C23, C27, C28) for all exposure scenarios (Table 5). All total edible crab tissue samples exceeded an excess cancer risk of 1×10^{-5} and the majority of samples under the 30 and 70-year scenarios exceeded a risk of 1×10^{-4} (Table 5). Excess cancer risk for crab muscle was substantially lower and exceeded 1×10^{-4} only at four locations under the 70-year exposure regime (Table 5). Oyster samples exhibited a risk profile (Table 6) similar to crabs, although several samples exceeded an excess cancer risk of 1×10^{-4} for the 70-year exposure. Dioxins/PCBs accounted for 85–99%, 60–90%, 27–94%, and 53–99% of the total excess cancer risk for crab hepatopancreas, total edible crab tissue, crab muscle, and oysters, respectively.

Non-carcinogenic health risks were evaluated for seven of the analyzed metals. Three of the metals were not included in the HI calculations because either none of the samples exceeded the detection limits (lead) or RfDs were not available (copper, tin). Cadmium was omitted from the HI calculations for crab muscle because all concentrations were below the detection limits. The majority of sampling locations exceeded an HI of 1.0 (Tables 5 and 6). Mercury accounted for 64–87% of the total HI in crab muscle, and thus the primary potential non-carcinogenic health effects would be neurological or reproductive. In crab hepatopancreas samples, mercury and cadmium accounted for the primary potential non-carcinogenic health effects of concern (neurological, reproductive, and renal). In two hepatopancreas samples (C4, C9), cardiovascular effects may be of concern due to levels of inorganic arsenic. Potential non-carcinogenic health effects in oysters based on total HI

Table 4
Dioxin/furan (pg g⁻¹), dioxin-like PCB (pg g⁻¹), and metals concentrations (mg kg⁻¹) in oyster samples

Congener	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10
2,3,7,8-TCDD	0.01	0.62	0.10	0.15	0.15	0.05	0.15	0.04	0.10	0.04
1,2,3,7,8-PeCDD	0.24	1.40	0.32	0.15	0.10	0.05	0.15	0.12	0.10	0.14
1,2,3,4,7,8-HxCDD	0.25	1.19	0.10	0.15	0.10	0.05	0.15	0.18	0.10	0.10
1,2,3,6,7,8-HxCDD	0.63	3.35	0.68	0.10	0.25	0.05	0.10	0.55	0.43	0.26
1,2,3,7,8,9-HxCDD	0.54	2.30	0.35	0.49	0.53	0.05	0.15	0.43	0.61	0.33
1,2,3,4,6,7,8-HpCDD	1.78	9.50	2.70	2.10	0.45	1.00	0.80	1.72	0.70	1.10
OCDD	15.10	52.05	23.50	15.80	10.40	9.20	13.80	14.30	8.60	16.80
2,3,7,8-TCDF	1.08	4.30	3.80	0.80	1.10	0.73	0.81	0.55	1.00	0.63
1,2,3,7,8-PeCDF	0.11	0.64	0.28	0.10	0.05	0.04	0.10	0.06	0.34	0.02
2,3,4,7,8-PeCDF	0.59	0.78	0.33	0.10	0.05	0.05	0.10	0.12	0.05	0.09
1,2,3,4,7,8-HxCDF	0.01	0.04	0.05	0.05	0.04	0.04	0.05	0.01	0.31	0.08
1,2,3,6,7,8-HxCDF	0.01	0.60	0.05	0.05	0.04	0.03	0.05	0.01	0.04	0.02
1,2,3,7,8,9-HxCDF	0.02	0.05	0.10	0.15	0.05	0.05	0.10	0.01	0.10	0.02
2,3,4,6,7,8-HxCDF	0.01	0.26	0.10	0.10	0.04	0.04	0.10	0.03	0.05	0.02
1,2,3,4,6,7,8-HpCDF	0.14	0.28	0.10	0.10	0.05	0.05	0.10	0.04	0.05	0.05
1,2,3,4,7,8,9-HpCDF	0.02	0.10	0.15	0.20	0.10	0.10	0.20	0.02	0.10	0.03
OCDF	0.34	0.35	0.40	0.40	0.20	0.15	0.40	0.18	0.25	0.10
TEQ _{DF}	0.83	3.75	1.15	0.57	0.50	0.24	0.52	0.42	0.52	0.38
PCB-77	34.5	258.0	41.5	46.5	47.8	31.4	34.7	60.7	72.4	19.4
PCB-81	2.10	48.00	7.30	8.50	9.40	5.70	6.90	2.55	17.90	6.50
PCB-105	206.0	1115.0	190.0	233.0	219.0	130.0	150.0	421.0	405.0	139.0
PCB-114	6.40	102.05	13.60	15.80	15.20	9.60	9.90	17.55	26.90	10.50
PCB-118	1130.0	3410.0	936.0	1180.0	1280.0	778.0	885.0	2115.0	2370.0	773.0
PCB-123	15.3	753.0	275.0	328.0	422.0	251.0	318.0	32.8	645.0	223.0
PCB-126	30.80	14.35	5.00	5.30	7.80	0.30	0.30	6.05	8.20	0.40
PCB-156/157	164.1	214.8	102.2	108.2	104.6	65.4	74.9	223.5	223.0	77.8
PCB-167	150.0	120.0	56.6	67.4	61.6	38.1	45.4	111.5	136.0	41.1
PCB-169	7.00	0.50	0.40	0.50	0.40	0.50	0.40	0.70	0.40	0.40
PCB-189	14.70	0.35	0.40	0.30	0.20	0.30	0.30	6.30	4.20	0.30
TEQ _P	3.38	2.16	0.71	0.78	1.04	0.19	0.22	1.00	1.30	0.20
As	1.80	1.15	1.40	0.97	1.90	2.60	2.30	0.12	1.60	2.50
In. As	0.018	0.012	0.014	0.010	0.019	0.026	0.023	0.001	0.016	0.025
Cd	0.61	0.15	0.05	0.17	0.04	0.11	0.03	0.08	0.05	0.43
Cr	0.17	0.02	0.14	0.07	0.07	0.07	0.06	0.15	0.08	0.71
Cu	56.0	44.5	13.0	6.7	1.5	5.8	1.3	10.5	4.9	6.7
Pb	0.42	0.04	0.21	0.17	0.17	0.16	0.14	0.37	0.20	0.12
Hg	0.017	0.040	0.060	0.050	0.051	0.06	0.055	0.028	0.051	0.025
Ni	0.25	0.02	0.13	0.10	0.10	0.10	0.09	0.69	0.12	0.07
Se	0.27	0.24	0.14	0.11	0.14	0.2	0.21	0.24	0.13	0.95
Sn	0.6	0.01	0.09	0.59	0.05	0.05	0.02	0.14	0.14	0.07
Zn	1000	850	190	290	62	130	21	165	200	190

Numbers in bold represent samples for which concentrations were below the detection limit (DL), and the concentration is expressed as DL/2. Locations correspond with those indicated on Fig. 1.

that exceeded 1.0 included metabolic effects from zinc, renal effects from cadmium, and reproductive or neurological effects due to mercury. However, it should be recognized that an HI > 1 does not necessarily indicate that toxicity is likely, but rather that an upper bound estimate of risk has been attained.

4. Discussion

4.1. Organic contaminants

Analysis of blue crab and oyster tissues demonstrates that elevated levels of bioavailable dioxins/furans and DL-PCBs exist in areas of the Pensacola Bay region. The elevated levels are particularly evident in crab and crab hepatopancreas samples taken in the urbanized bayous in the city of Pensacola

and along the western edge of Escambia Bay. However, crab samples from several locations, including Perdido and East/Blackwater Bays, exhibited consistently lower levels of contamination. Similar patterns were observed in oyster tissues — those samples collected in urbanized areas exhibited the highest TEQ_{DFP}. These results reflect known spatial distributions of contaminants in sediments of these estuaries (Brim, 1993; Debusk et al., 2002; Hemming et al., 2003). The PCA analysis confirmed that the congener profiles in the tissue samples were not ubiquitous and clustered based on these regional contamination patterns. Of the three tissues sampled, crab muscle exhibited the lowest levels of contamination, which reflects its lower lipid content relative to hepatopancreas and oyster tissue. In general, because of their direct contact with sediment and diet of mostly benthic organisms,

O11	O12	O13	O14	O15	O16	O17	O18	O19	O20	O21	O22	O23
0.02	0.10	0.10	0.10	0.10	0.05	0.05	0.02	0.03	0.02	0.03	0.02	0.03
0.03	0.10	0.10	0.10	0.10	0.10	0.15	0.05	0.04	0.05	0.04	0.05	0.15
0.05	0.10	0.10	0.10	0.10	0.27	0.10	0.05	0.05	0.14	0.09	0.08	0.18
0.10	0.15	0.15	0.59	0.10	0.20	0.30	0.15	0.24	0.24	0.21	0.19	0.52
0.26	0.10	0.15	0.65	0.10	0.20	0.30	0.33	0.30	0.15	0.22	0.21	0.52
1.00	1.60	0.25	1.40	0.50	1.40	0.70	1.00	1.10	0.74	1.20	0.87	1.55
11.80	16.90	5.80	6.15	10.10	10.60	12.20	8.70	9.60	6.20	12.70	9.60	11.70
0.43	0.46	0.05	0.99	0.65	0.99	0.90	0.30	0.36	0.34	0.15	0.15	0.45
0.02	0.05	0.05	0.10	0.05	0.05	0.30	0.02	0.02	0.02	0.02	0.02	0.29
0.04	0.05	0.05	0.10	0.05	0.05	0.10	0.11	0.05	0.02	0.12	0.12	0.16
0.02	0.10	0.10	0.05	0.05	0.04	0.05	0.07	0.05	0.07	0.03	0.07	0.04
0.02	0.05	0.05	0.05	0.05	0.04	0.04	0.02	0.02	0.06	0.02	0.05	0.02
0.02	0.10	0.10	0.10	0.05	0.05	0.10	0.02	0.03	0.02	0.03	0.07	0.03
0.02	0.10	0.10	0.05	0.05	0.05	0.05	0.02	0.02	0.02	0.03	0.05	0.03
0.02	0.10	0.10	0.05	0.05	0.05	0.05	0.06	0.04	0.06	0.09	0.04	0.03
0.03	0.20	0.20	0.15	0.10	0.10	0.15	0.03	0.04	0.03	0.03	0.03	0.05
0.05	0.35	0.40	0.25	0.20	0.25	0.35	0.12	0.24	0.05	0.05	0.10	0.06
0.16	0.36	0.31	0.53	0.35	0.38	0.46	0.23	0.21	0.19	0.21	0.23	0.41
34.3	30.0	21.0	30.2	32.2	25.6	65.5	16.2	11.4	13.0	9.2	6.6	22.5
7.50	7.50	0.70	6.40	7.50	6.10	3.80	3.80	2.50	3.00	0.50	0.20	0.73
181.0	147.0	102.0	159.0	190.0	135.0	83.0	88.6	61.0	56.0	50.3	29.1	111.7
12.60	9.70	8.20	10.60	11.00	9.70	4.60	5.20	4.10	0.40	0.60	0.30	2.87
833.0	793.0	541.0	837.0	1100.0	698.0	386.0	469.0	325.0	299.0	231.0	150.0	543.7
264.0	258.0	188.0	272.0	387.0	243.0	120.0	157.0	114.0	106.0	89.4	47.6	34.5
0.90	0.90	1.10	4.30	3.10	3.90	6.40	0.30	0.30	0.40	0.70	0.30	5.67
93.2	66.1	50.6	86.2	108.4	85.1	48.0	50.2	36.2	27.6	20.7	12.6	57.3
47.8	42.0	30.7	48.9	63.7	44.6	24.7	24.4	18.4	17.2	10.7	7.8	29.4
1.60	1.30	1.70	0.50	0.60	0.40	0.40	0.40	0.40	0.50	0.80	0.30	0.47
1.40	1.10	1.60	0.40	0.50	0.30	0.30	0.30	0.30	0.30	0.60	0.30	1.43
0.29	0.26	0.24	0.61	0.55	0.55	0.74	0.13	0.10	0.10	0.12	0.06	0.74
2.20	2.80	2.50	1.10	2.00	1.90	2.20	2.20	2.90	2.10	2.10	2.30	1.73
0.022	0.028	0.025	0.011	0.020	0.019	0.022	0.022	0.029	0.021	0.021	0.023	0.017
0.36	0.32	0.59	0.28	0.04	0.05	0.10	0.44	0.59	0.50	0.44	0.35	0.50
0.46	0.41	0.33	0.11	0.07	0.08	0.23	0.46	0.84	0.51	0.53	0.5	0.67
6.3	10.0	24.0	2.6	4.2	3.0	5.6	7.4	8.5	9.5	6.9	8.1	8.0
0.13	0.12	0.12	0.14	0.18	0.19	0.15	0.10	0.12	0.10	0.11	0.11	0.23
0.020	0.018	0.016	0.02	0.074	0.070	0.05	0.011	0.006	0.017	0.024	0.030	0.020
0.08	0.07	0.07	0.09	0.11	0.12	0.09	0.06	0.07	0.20	0.07	0.06	0.14
0.61	0.72	1.30	0.21	0.12	0.13	0.28	0.86	0.87	0.80	0.79	0.91	0.94
0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.04	0.09	0.09	0.12	0.12	0.30
130	200	340	1000	1200	440	110	150	120	190	160	190	170

crabs are expected to contain higher levels of dioxins and PCBs than filter-feeders such as oysters (Ylitalo et al., 1999).

Direct comparisons of our data with those from other studies were complicated by differences in TEQ calculation method (International-TEQ vs. WHO-TEQ), use of various substitution methods for concentrations that are below detection limit, higher detection limits in previous studies, and exclusion of either dioxins/furans or DL-PCBs from the analyses. Previous studies that reported TEQ_{DFP} for oysters or blue crabs could not be identified. Likewise, few studies of blue crabs and oysters reported congener-specific data, which could have allowed for recalculation of TEQs using the WHO method, and most studies reported PCB concentrations as total PCBs. In studies where detailed data were provided, we recalculated TEQs to enable comparisons to our data.

Ylitalo et al. (1999) reported DL-PCBs in blue crabs collected from several locations along the east coast of the United States, the majority of which were located either within or just downstream of urban areas. Although mean TEQ_P in crab hepatopancreas samples in the present study from the urbanized bayous and western Escambia Bay were lower than mean TEQ_P reported by Ylitalo et al. (1999) for samples from Baltimore Harbor, MD (24 pg g⁻¹) and the St. John’s River, FL (83 pg g⁻¹), the maximum concentrations from the most contaminated locations in the present study fell within the range observed in Baltimore Harbor. The hepatopancreas samples from the urban bayous, western Escambia Bay, and eastern Escambia Bay exceeded the mean concentrations reported by Ylitalo et al. (1999) for three other locations along the lower east coast of the United States that are considered urban-impacted areas (Charleston Harbor, SC; Cape Fear River, NC;

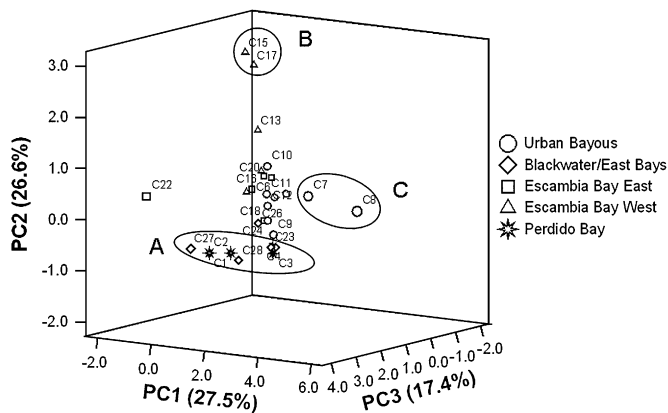


Fig. 2. Factor scores plot from principal components analysis of dioxin/furan and DL-PCB congeners in crab muscle samples. The variance accounted for by the first three principal components (PC) is shown in brackets. Sample designations correspond to locations on Fig. 1 and in Table 1.

and Savannah River, GA). Hepatopancreas samples from the areas in the present study with lower levels of industrial or urban development (Perdido Bay and East/Blackwater Bay) also exceeded TEQ_P from comparable locations reported by Ylitalo et al. (Sapelo Sound, GA and Chester River, MD). However, because none of their samples exceeded the detection limit for PCB 126, Ylitalo et al. did not include PCB126 in their TEQ_P calculations. Due to its high TEF value (0.1), PCB126 accounted for 44–87% of our $TEQs$ in crab hepatopancreas and muscle samples. Therefore, the TEQ_P calculated by Ylitalo et al., likely underestimated the actual TEQ_P in their study. TEQ_P for crab muscle samples collected from the urbanized bayous and western and eastern Escambia Bay also exceeded all mean crab muscle TEQ_P reported by Ylitalo et al. (1999) for samples collected in urbanized areas. However, the crab muscle samples we collected from the less developed areas (Blackwater/East Bays and Perdido Bay) exhibited similar TEQ_P to those reported by Ylitalo et al. (1999) at comparable locations.

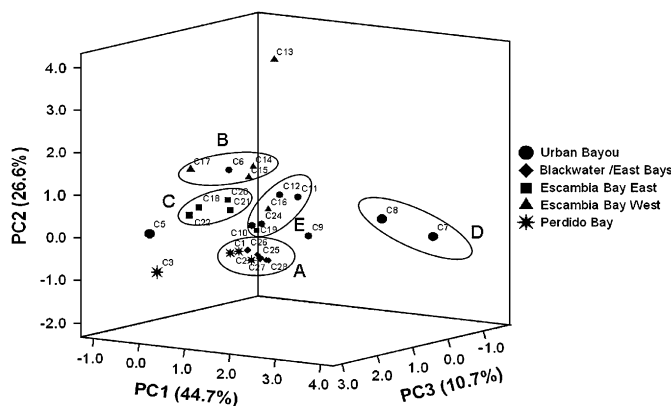


Fig. 3. Principal components analysis of dioxin/furan and DL-PCB congeners in crab hepatopancreas. Factor scores plot shows the variance accounted for by the first three principal components (PC) in brackets. Five major clusters were identified by the analysis. Sample designations correspond to locations on Fig. 1 and in Table 1.

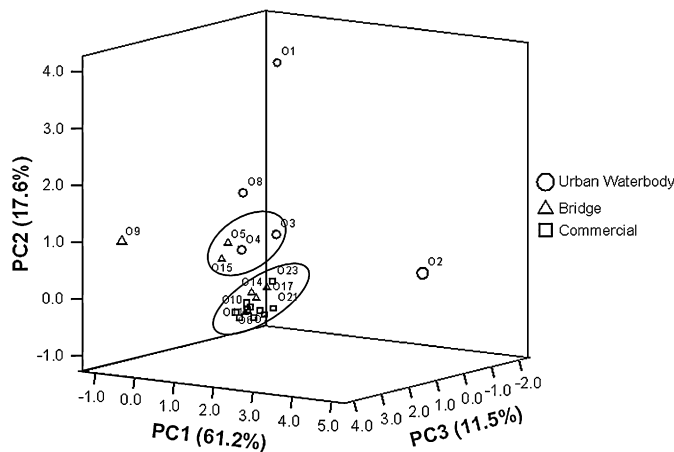


Fig. 4. Principal components factor scores plot of dioxin/furan and DL-PCB congeners in oyster tissues. The variance accounted for by the first three principal components (PC) is shown in brackets. Sample designations correspond to locations on Fig. 1 and in Table 1.

The highest TEQ_{DF} for crab hepatopancreas samples from the most contaminated locations within the Pensacola Bay region (urban bayous) were between five and ten fold lower than TEQ_{DF} for data reported for an urbanized river in the New York/New Jersey Harbor Estuary (Lower Raritan River) by Ashley and Horwitz (2002) ($106.9\text{--}210.9\text{ pg g}^{-1}$; $ND = 0$) and by Iannuzzi et al. (2004) for the lower Passaic River ($210\text{--}410\text{ pg g}^{-1}$; $ND = DL/2$). Maximum TEQ_{DF} for crab muscle samples from the urban bayous in the Pensacola Bay region were also lower than nearly all samples from the Lower Raritan River ($0.0\text{--}7.9\text{ pg g}^{-1}$; $ND = 0$) and lower Passaic River ($30\text{--}150\text{ pg g}^{-1}$; $ND = DL/2$). The range of TEQ_{DF} ($0.002\text{--}1.00\text{ pg g}^{-1}$ $ND = 0$ and $0.043\text{--}1.002\text{ pg g}^{-1}$ $ND = DL/2$) reported by Jensen and Bolger (2001) for blue crab muscle tissue collected from 500 retailers across the United States also exhibited higher maxima and mean levels than we observed in any of our sample groups.

Sericano et al. (1994) reported TEQ_P for oysters collected from Galveston Bay, TX, and Tampa Bay, FL, two highly urbanized watersheds. The majority of samples from these locations exhibited higher TEQ_P ($2.7\text{--}55.5\text{ pg g}^{-1}$ and $0.3\text{--}14.5\text{ pg g}^{-1}$, respectively) than those reported here for urban sampling locations. Jensen and Bolger (2001) sampled oysters from retailers across the United States and reported TEQ_{DF} ($0.11\text{--}0.898\text{ pg g}^{-1}$, mean 0.442 pg g^{-1} $ND = 0$ and $0.14\text{--}0.901\text{ pg g}^{-1}$, mean 0.448 pg g^{-1} $ND = DL/2$) that were higher than the maxima and mean TEQ_{DF} in oysters collected from commercial oyster beds and bridges in the Pensacola Bay region. Likewise, our commercial oyster bed and bridge samples had lower TEQ_{DF} than oysters collected by Fiedler et al. (1997) from seafood markets in southern Mississippi ($0.65\text{--}0.79\text{ pg g}^{-1}$, mean 0.69 pg g^{-1} , $ND = DL/2$). However, both mean and maximum TEQ_{DF} of samples collected from the urban waterways in the Pensacola region exceeded those reported by Jensen and Bolger (2001) and Fiedler et al. (1997) by two to five fold.

Table 5

Excess cancer risks and non-cancer risks (HI) associated with consumption of crab muscle, crab hepatopancreas and total edible crab tissue collected from the Pensacola Bay region

Location	Station ID	Crab muscle				Hepatopancreas				Total edible crab tissue			
		70 yr	30 yr	9 yr	HI	70 yr	30 yr	9 yr	HI	70 yr	30 yr	9 yr	HI
Perdido-11 Mile Creek	C1	3.6E-05	1.6E-05	4.7E-06	1.2	8.9E-04	3.8E-04	1.1E-04	0.9	1.6E-04	7.1E-05	2.1E-05	1.2
Perdido Bay – Upper	C2	4.0E-05	1.7E-05	5.1E-06	1.4	9.4E-04	4.0E-04	1.2E-04	0.7	1.8E-04	7.5E-05	2.3E-05	1.3
Perdido Bay – Lillian Bridge	C3	2.2E-05	9.5E-06	2.9E-06	2.0	1.3E-03	5.6E-04	1.7E-04	2.2	2.2E-04	9.2E-05	2.8E-05	2.0
Perdido Bay – Tarkiln Bayou	C4	4.5E-05	1.9E-05	5.8E-06	1.3	9.0E-04	3.9E-04	1.2E-04	1.9	1.7E-04	7.4E-05	2.2E-05	1.4
Bayou Grande Upper	C5	7.7E-05	3.3E-05	1.0E-05	1.1	1.7E-03	7.5E-04	2.2E-04	2.0	3.3E-04	1.4E-04	4.2E-05	1.3
Bayou Grande	C6	7.5E-05	3.2E-05	9.6E-06	1.1	3.0E-03	1.3E-03	3.8E-04	3.9	5.1E-04	2.2E-04	6.5E-05	1.6
Bayou Chico Upper	C7	1.1E-04	4.5E-05	1.4E-05	0.7	4.0E-03	1.7E-03	5.2E-04	0.7	6.9E-04	3.0E-04	8.9E-05	0.7
Bayou Chico Bridge	C8	1.1E-04	4.5E-05	1.4E-05	1.2	3.2E-03	1.4E-03	4.1E-04	1.4	5.7E-04	2.5E-04	7.4E-05	1.3
Bayou Chico Mouth	C9	1.3E-04	5.6E-05	1.7E-05	1.4	2.0E-03	8.6E-04	2.6E-04	2.7	4.1E-04	1.8E-04	5.3E-05	1.6
Bayou Texar Upper	C10	6.9E-05	2.9E-05	8.8E-06	1.7	1.4E-03	6.1E-04	1.8E-04	3.6	2.7E-04	1.2E-04	3.5E-05	2.0
Bayou Texar Mid	C11	4.1E-05	1.7E-05	5.2E-06	1.2	2.6E-03	1.1E-03	3.4E-04	1.2	4.3E-04	1.8E-04	5.5E-05	1.2
Bayou Texar Mouth	C12	3.7E-05	1.6E-05	4.7E-06	1.3	1.8E-03	7.7E-04	2.3E-04	2.0	3.0E-04	1.3E-04	3.9E-05	1.5
Gaberonne	C13	1.1E-04	4.7E-05	1.4E-05	1.7	3.4E-03	1.5E-03	4.4E-04	9.0	6.1E-04	2.6E-04	7.8E-05	2.8
Devils Point	C14	4.0E-05	1.7E-05	5.1E-06	1.2	1.7E-03	7.5E-04	2.2E-04	2.6	2.9E-04	1.2E-04	3.7E-05	1.4
Escambia Bay NW	C15	8.5E-05	3.7E-05	1.1E-05	1.5	1.5E-03	6.5E-04	1.9E-04	2.2	3.0E-04	1.3E-04	3.8E-05	1.6
Mackey Cove	C16	4.5E-05	1.9E-05	5.7E-06	1.2	1.0E-03	4.3E-04	1.3E-04	1.4	1.9E-04	8.0E-05	2.4E-05	1.2
Escambia Channel	C17	8.2E-05	3.5E-05	1.1E-05	1.5	1.9E-03	8.4E-04	2.5E-04	1.2	3.6E-04	1.6E-04	4.7E-05	1.5
Escambia Bay NE	C18	3.5E-05	1.5E-05	4.5E-06	1.1	1.5E-03	6.6E-04	2.0E-04	1.1	2.6E-04	1.1E-04	3.3E-05	1.1
Mulat Bayou	C19	5.1E-05	2.2E-05	6.5E-06	0.8	8.6E-04	3.7E-04	1.1E-04	4.7	1.7E-04	7.3E-05	2.2E-05	1.4
Indian Bayou	C20	5.2E-05	2.2E-05	6.7E-06	1.3	1.6E-03	6.7E-04	2.0E-04	1.5	2.8E-04	1.2E-04	3.6E-05	1.3
Trout Bayou	C21	5.3E-05	2.3E-05	6.8E-06	1.7	2.2E-03	9.3E-04	2.8E-04	1.8	3.7E-04	1.6E-04	4.8E-05	1.8
Escambia Bay SE	C22	8.6E-05	3.7E-05	1.1E-05	1.0	1.6E-03	6.8E-04	2.0E-04	1.2	3.1E-04	1.3E-04	4.0E-05	1.1
Garcon Point	C23	5.0E-05	2.1E-05	6.4E-06	1.7	3.7E-04	1.6E-04	4.8E-05	2.0	9.9E-05	4.2E-05	1.3E-05	1.8
Hoffman Bayou	C24	5.3E-05	2.3E-05	6.8E-06	1.3	1.3E-03	5.7E-04	1.7E-04	1.5	2.5E-04	1.1E-04	3.2E-05	1.3
Redfish Point	C25	5.1E-05	2.2E-05	6.6E-06	1.4	1.9E-03	8.0E-04	2.4E-04	1.7	3.2E-04	1.4E-04	4.2E-05	1.5
East River	C26	5.7E-05	2.4E-05	7.3E-06	1.1	1.1E-03	4.6E-04	1.4E-04	1.8	2.1E-04	9.0E-05	2.7E-05	1.2
Yellow River	C27	6.1E-05	2.6E-05	7.8E-06	1.2	4.1E-04	1.8E-04	5.3E-05	1.5	1.1E-04	4.6E-05	1.4E-05	1.3
Blackwater Bay	C28	4.1E-05	1.7E-05	5.2E-06	1.6	4.2E-04	1.8E-04	5.4E-05	1.3	1.0E-04	4.5E-05	1.3E-05	1.6

Exposure duration (9 yr, 30 yr, 70 yr) was varied in the calculation of cancer-risks to account for the effects of residence time on consumption risks.

Table 6
Excess cancer risks and non-cancer risks (HI) associated with consumption of oysters collected from the Pensacola Bay region

Location	Station ID	Oysters			HI
		70 yr	30 yr	9 yr	
Bayou Grande	O1	4.5E-04	1.9E-04	5.8E-05	2.8
Bayou Chico Bridge	O2	6.2E-04	2.6E-04	7.9E-05	2.3
Bayfront Auditorium	O3	2.0E-04	8.8E-05	2.6E-05	0.9
Bayou Texar	O4	1.5E-04	6.3E-05	1.9E-05	1.1
Pensacola Bay Bridge North	O5	1.8E-04	7.6E-05	2.3E-05	0.6
Pensacola Bay Bridge Mid	O6	7.0E-05	3.0E-05	9.0E-06	0.9
Pensacola Bay Bridge South	O7	9.8E-05	4.2E-05	1.3E-05	0.5
Gaberonne	O8	1.5E-04	6.3E-05	1.9E-05	0.7
I-10 Bridge Mid	O9	2.0E-04	8.7E-05	2.6E-05	0.9
Escambia Bay 7	O10	8.5E-05	3.6E-05	1.1E-05	1.2
Escambia Bay 1	O11	6.8E-05	2.9E-05	8.8E-06	0.9
Escambia Bay 5	O12	9.2E-05	3.9E-05	1.2E-05	1.0
Escambia Bay 8	O13	8.2E-05	3.5E-05	1.0E-05	1.5
Garcon Point Bridge North	O14	1.3E-04	5.5E-05	1.6E-05	2.6
Garcon Point Bridge Mid	O15	1.1E-04	4.8E-05	1.4E-05	3.2
Garcon Point Bridge South	O16	1.1E-04	4.9E-05	1.5E-05	1.5
Bob Sikes Bridge Mid	O17	1.4E-04	6.2E-05	1.9E-05	0.8
East Bay 13	O18	5.9E-05	2.5E-05	7.6E-06	1.0
East Bay 2	O19	6.0E-05	2.6E-05	7.8E-06	1.1
East Bay 3	O20	5.1E-05	2.2E-05	6.5E-06	1.1
East Bay 5	O21	5.5E-05	2.4E-05	7.1E-06	1.1
East Bay 8	O22	5.2E-05	2.2E-05	6.7E-06	1.1
East Bay 9	O23	1.4E-04	6.1E-05	1.8E-05	1.1

Exposure duration (9 yr, 30 yr, 70 yr) was varied in the calculation of cancer risks to account for the effects of residence time on consumption risks.

4.2. Inorganic contaminants

Although many metals are released naturally into the environment through weathering and leaching processes, human activities have modified the budgets of these elements in estuaries and coastal waters such that levels in fish and shellfish pose a threat to human consumers. Levels of certain metals in the present study reflected regional patterns of sediment contamination. For example, copper in hepatopancreas and oysters, and cadmium in hepatopancreas were highest in urban bayous, which contain the highest sediment levels of metals (Debusk et al., 2002). Similarly, hepatopancreas copper concentrations were generally higher in western Escambia Bay than eastern, also reflecting sediment levels (Debusk et al., 2002).

Although both organic and inorganic arsenic species are present in marine tissues, inorganic arsenic is substantially more toxic to humans (U.S. EPA, 2000). In the present study, consumption of crab hepatopancreas would present the highest health risk from inorganic arsenic. However, crab muscle and oysters from select locations may also be a significant source. To date, most studies of contamination in marine species have focused on total arsenic concentrations and therefore few data are available on inorganic arsenic levels in blue crabs and eastern oysters. Higher than national average total arsenic levels have been previously reported at many locations in the southeastern U.S. and Gulf Coast in sediments and oysters as a result of elevated natural and anthropogenic inputs (Valette-Silver et al., 1999). According to the National Status and

Trends (NST) Mussel Watch Project, the national NST mean for total arsenic is $11.1 \pm 3.4 \text{ mg kg}^{-1}$ dry weight (ca. $1.65 \pm 0.5 \text{ mg kg}^{-1}$ wet weight) and contamination in oysters is considered “high” when arsenic levels are above 14.5 mg kg^{-1} dry weight (ca. 2.15 mg kg^{-1} wet weight) (Valette-Silver et al., 1999). Although a number of sampling locations in the present study exceeded these national levels, all of our samples were below the NST mean concentration for the southeast coast of the U.S. ($25.4 \pm 10.4 \text{ mg kg}^{-1}$ dry weight, ca. $3.77 \pm 1.5 \text{ mg kg}^{-1}$ wet weight). Mean total arsenic concentrations in all crab muscle and hepatopancreas sample groups in the present study exceeded those reported by Jop et al. (1997) for two urbanized estuaries in Connecticut and also exceeded those reported by Ju and Harvey (2002) for a reference site in Maryland. Crab muscle and hepatopancreas samples from Perdido Bay, the urban bayous and East/Blackwater Bay also exhibited higher mean total arsenic levels than two urbanized sites near Baltimore, MD (Ju and Harvey, 2002).

With few exceptions, crab muscle samples collected in the present study exhibited the highest levels of mercury. Because of their trophic status, crabs are expected to bioaccumulate higher levels of mercury than oysters. Mercury was unique among the monitored contaminants in that higher concentrations were found in muscle relative to hepatopancreas. In general, the mercury concentrations in crab muscle and hepatopancreas exceeded those observed in the northeastern U.S. (Eisenberg and Topping, 1984; Iannuzzi et al., 2004; Jop et al., 1997; Ju and Harvey, 2002). However, other locations along the Gulf of Mexico with comparable land use features and annual rainfall amounts exhibited similar mercury levels in crab muscle to those reported here (Ache et al., 2000). The levels of mercury in oysters from the present study fell within the range reported previously for locations along the Florida Panhandle ($0.008\text{--}0.37 \text{ mg kg}^{-1}$) (Ache et al., 2000; Lewis et al., 2004; Oliver et al., 2001). However, they generally exceeded the NST national median concentration (0.015 mg kg^{-1} wet weight), and mean levels in samples from the urban waterways and bridges exceeded the NST 85th percentile (0.034 mg kg^{-1} wet weight) (O'Connor, 2002). The Mercury Deposition Network has previously reported that the station with the second highest recorded level ($26.8 \mu\text{g/m}^2$) of wet deposition of total mercury in the U.S. was located in Baldwin County, AL, which is the closest station to Pensacola Bay (NADP, 2004). Therefore, the higher levels in samples from our study are not unexpected.

4.3. Risks to consumers

In general, blue crab hepatopancreas contained the highest levels of dioxin/furan/DL-PCBs and metals such as arsenic, copper and cadmium. Consumers who do not deliberately eat the hepatopancreas can still be exposed to its contaminants if crabs are cooked whole because contaminants in the hepatopancreas are transferred to cooking liquid and muscle tissue. Likewise, inclusion of hepatopancreas concentrations in the estimates of total edible crab tissue resulted in a greater

number of SV exceedences compared to crab muscle alone. These results suggest that despite accounting for a small fraction of total edible tissues in blue crabs, the contaminant burdens in hepatopancreas significantly increase the risk to humans who consume all soft crab tissues. Many states, including Maryland, New York, New Jersey, and Washington, have issued consumption advisories specifically for crab hepatopancreas (U.S. EPA, 2003), and based on the results from the present study, a similar advisory may be warranted for blue crabs in the Pensacola Bay region.

4.4. Conclusions

We found that oysters and blue crabs from several locations in the Pensacola Bay region contain levels of contaminants that may pose a risk to human consumers, based on exceedence of calculated screening values and elevated health risk indices. In general, shellfish collected from urbanized waterbodies including the bayous within the city of Pensacola and from locations in western Escambia Bay exhibited the highest levels of contaminants. PCA confirmed that dioxin/furan and DL-PCB congener patterns vary throughout the sampling area and reflect contaminant source locations. From a human health perspective, the results of this study emphasize the need to monitor all 29 dioxin/furan/DL-PCB congeners whenever the potential toxicity from consumption of dioxin-like compounds is assessed in fish or shellfish.

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References

- Ache, B.W., Boyle, J.D., Morse, C.E., 2000. A Survey of the Occurrence of Mercury in the Fishery Resources of the Gulf of Mexico. U.S. EPA Gulf of Mexico Program.
- Ashley, J., Horwitz, R.J., 2002. New Jersey survey of fish and shellfish tissue for the evaluation of spatial trends and human health impacts. A supplemental study to the assessment of PCBs, selected organic pesticides and mercury in fishes from New Jersey: 1998–1999 monitoring program. Academy of Natural Sciences, 02–13.
- Brim, M., 1993. Toxics Characterization Report for Perdido Bay, Alabama and Florida. U.S. Fish and Wildlife Service. PCFO-EC-93–04.
- Clark, J., Patrick, J., Moore, J., Forester, J., 1986. Accumulation of sediment-bound PCBs by fiddler crabs. Bulletin of Environmental Contamination and Toxicology 36, 571–578.
- Debusk, W., Poyer, I., Herzfeld, I., 2002. Sediment Quality in the Pensacola Bay System. Northwest Florida Water Management District. Technical File Report 02-03.
- Degner, R.L., Adams, C.M., Moss, S.D., Mack, S.K., 1994. Per Capita Fish and Shellfish Consumption in Florida. Florida Agricultural Market Research Center, Institute of Food and Agricultural Sciences, University of Florida.
- Eisenberg, M., Topping, J.J., 1984. Trace metal residues in shellfish from Maryland waters. Journal of Environmental Science and Health B19, 649–671.
- Fairey, R., Taberski, K., Lamerdin, S., Johnson, E., Clark, R., Downing, J., Newman, J., Petreas, M., 1997. Organochlorines and other environmental contaminants in muscle tissues of sportfish collected from San Francisco Bay. Marine Pollution Bulletin 34, 1058–1071.
- Fiedler, H., Cooper, K., Bergek, S., Hjelt, M., Rappe, C., 1997. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) in food samples collected in southern Mississippi, USA. Chemosphere 34, 1411–1419.
- Hemming, J., Brim, M., Jarvis, R., 2003. A survey of dioxin and furan compounds in sediments of Florida Panhandle bay systems. Marine Pollution Bulletin 46, 491–521.
- Iannuzzi, T.J., Armstrong, T.N., Thelen, J.B., Ludwig, D.F., 2004. Chemical contamination of aquatic organisms from an urbanized river in the New York/New Jersey Harbor estuary. Human and Ecological Risk Assessment 10, 389–413.
- Jensen, E., Bolger, P., 2001. Exposure assessment of dioxins/furans consumed in dairy foods and fish. Food Additives and Contaminants 18, 395–403.
- Jop, K., Biever, R., Hoberg, J., Shepherd, S., 1997. Analysis of metals in blue crabs, *Callinectes sapidus*, from two Connecticut estuaries. Bulletin of Environmental Contamination and Toxicology 58, 311–317.
- Ju, S.-J., Harvey, H.R., 2002. Effects of temperature and heavy metals on extractable lipofuscin in the blue crab, *Callinectes sapidus*. Journal of the Korean Society of Oceanography 37, 1–10.
- Lewis, M., Quarles, R.L., Dantin, D.D., Moore, J.C., 2004. Evaluation of a Florida coastal golf complex as a local and watershed source of bioavailable contaminants. Marine Pollution Bulletin 48, 254–262.
- NADP, 2004. National Atmospheric Deposition Program 2003 Annual Summary. National Atmospheric Deposition Program (NADP), Illinois State Water Survey. NADP Data Report 2004–01.
- NJDEP, 2002. Estimate of Cancer Risk To Consumers of Crabs Caught In The Area of the Diamond Alkali Site and Other Areas of the Newark Bay Complex From 2,3,7,8-TCDD and 2,3,7,8-TCDD Equivalents. New Jersey Department of Environmental Protection.
- O'Connor, T.P., 2002. National distribution of chemical concentrations in mussels and oysters in the USA. Marine Environmental Research 53, 117–143.
- Oliver, L., Fisher, W., Winstead, J., Hemmer, B., Long, E., 2001. Relationships between tissue contaminants and defense-related characteristics of oysters (*Crassostrea virginica*) from five Florida bays. Aquatic Toxicology 55, 202–222.
- Parrar, M.N., Hodges, P.B., John, E.V., Richard, W.R., Wheeler, E.P., 1969. Report of Arochlor Ad-hoc Committee. Monsanto Chemical Co.
- Sericano, J.L., Safe, S.H., Wade, T.L., Brooks, J.M., 1994. Toxicological significance of non-, mono- and di-ortho substituted polychlorinated biphenyls in oysters from Galveston and Tampa Bays. Environmental Toxicology and Chemistry 13, 1797–1803.
- Smith, A., Gangolli, S., 2002. Organochlorine chemicals in seafood: occurrence and health concerns. Food and Chemical Toxicology 40, 767–779.
- Tetra Tech NUS, I., 2003. Final Five Year Review, Naval Air Station Pensacola, Pensacola, FL. Southern Division, Naval Facilities Engineering Command.
- Thorpe, P., Bartel, R., Ryan, P., Albertson, K., Pratt, T., Cairns, D., 1997. The Pensacola Bay System Surface Water Improvement and Management Plan. Northwest Florida Water Management District.
- Tsai, D.E., Chen, H.-C., Tsai, C.-F., 1984. Total lipid and cholesterol content in the blue crab, *Callinectes sapidus* Rathbun. Comparative Biochemistry and Physiology 78B, 27–31.
- U.S. EPA, 1999. Ecological Condition of Estuaries in the Gulf of Mexico. Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division. 620-R-98–004.
- U.S. EPA, 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Fish Sampling and Analysis. US EPA. EPA-823-B-00–007.

- U.S. EPA, 2002. Columbia River Basin Fish Contaminant Survey 1996–1998. U.S. Environmental Protection Agency, Region 10. EPA 910-R-02–006.
- U.S. EPA, 2003. Update: National Listing of Fish and Wildlife Advisories. United States Environmental Protection Agency, Office of Water. EPA-823-F-03–003.
- Valette-Silver, N.J., Riedel, G.F., Crecelius, E.A., Windom, H., Smith, R.G., Dolvin, S.S., 1999. Elevated arsenic concentrations in bivalves from the southeast coasts of the USA. *Marine Environmental Research* 48, 311–333.
- Van den Berg, M., Birnbaum, L., Bosveld, A., Brunstrom, B., Cook, P., Feeley, M., Giesy, J., Hanberg, A., Hasegawa, R., Kennedy, S., Kubiak, T., Larsen, J., Rolaf van Leeuwen, F., Liem, A., Nolt, C., Peterson, R., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* 106, 775–792.
- Weis, J., Weis, P., 1992. Transfer of contaminants from CCA-treated lumber to aquatic biota. *Journal of Experimental Marine Biology and Ecology* 161, 189–199.
- Ylitalo, G., Buzitis, J., Krahn, M., 1999. Analysis of tissues of eight marine species from Atlantic and Pacific coasts for dioxin-like chlorobiphenyls (CBs) and total CBs. *Archives of Environmental Contamination and Toxicology* 37, 205–219.