Levels of Toxic Polychlorinated Biphenyls , Dibenzo-p-dioxins and Dibenzofurans in Biotic and Abiotic Samples from Galveston Bay, Texas U.S.A.

Piero R. Gardinali, and Terry L. Wade

Geochemical and Environmental Research Group
College of Geosciences and Maritime Studies
Texas A&M University
833 Graham Road, College Station, Texas 77845. U.S.A.

Introduction

A vast number of anthropogenic compounds have been released to the global environment from human activities. Among these are synthetic halogenated aromatic hydrocarbons (HAH) which are extremely persistent[1], widely distributed in the environment [2] and, due to their high hydrophobicity, exhibit potential for bioaccumulation and biomagnification. [3] In recent years, increasing attention has been focused on measuring HAHs in marine coastal environments and especially in fish and shellfish harvested from these waters. In general, many of the contaminants introduced originally in the water or deposited from the atmosphere have a high affinity for the particulate phase and sediments generally constitute a major sink for lipophilic organic contaminants. However, because sediments are also a biological habitat, food web uptake of these toxicants is strongly influenced and driven by their presence in the abiotic compartment. The toxicological and environmental chemistry of polychlorinated biphenyls (PCBs), dibenzo-p- dioxins (PCDD) and dibenzofurans (PCDF) has been extensively investigated. [4-5] Among the HAHs, in addition to the PCDDs and PCDFs, are the AHH active PCB congeners. These compounds, which resemble 2,3,7,8-TCDD in their mechanism of action, have been widely recognized as responsible for many of the adverse effects observed in wildlife. Since AHH active PCBs may be found in environmental samples at levels orders of magnitude greater than PCDD/Fs, their presence can not be neglected when establishing the risk associated with 'dioxin like" contaminants. However, the analysis of the most toxic and thus more relevant PCBs has been generally limited to the determination of the planar or non-ortho congeners and some of their mono-ortho derivatives [6-7] . This investigation reports the determination of di-mono- and non-ortho PCB congeners as well as the seventeen 2,3,7,8-substituted PCDD/PCDF in sediments and selected organism from Galveston Bay , Texas.

Experimental

Surficial sediment samples were collected from a small boat using a hand held box coring device at depths ranging from 2 to 3 meters. All efforts were made to sample fine grained sediments from every station. After collection, all sediments were stored in clean combusted glass containers and kept

refrigerated until arrival at the lab. All samples where then logged in and frozen until the time of analysis. American Oysters (*Crassostrea virginica*), Blue Crabs (*Callinectes sapidus*), and Hardhead Catfishes (*Arius felis*) were collected by manual dredging, gill net and hook and line, respectively. All organisms were dissected and the section of tissue to be analyzed was homogenized and kept frozen at -20°C until time of analysis. Collection was conducted in Galveston Bay, Texas at or near five locations regularly sampled for the NOAA Status and Trends Program : Carancahua Reef (GBCR), an oyster reef located in East Bay, Hanna's Reef (GBHR), a large commercial oyster reef located in West Bay, Todd's Dump (GBTD), a small oyster reef off Eagle Point, the Houston Yacht Club (GBYC), and the Houston Ship Channel (GBSC) near Morgan's point in Tabb's Bay (Figure 1). The analytical protocol used for the separation and determination of the targeted analytes was described elsewhere.[8] Briefly, biological tissues were extracted by macerating them with methylene chloride using a tissue homogenizer while sediments were extracted with toluene using a sohxlet - dean stark (SDS) assembly. To eliminate interferences caused by lipid material, the hexane extract was treated with a mixture of concentrated sulfuric acid and silica gel. The sample extracts were further purified by mixed-bed silica column chromatography (8 g of 44% sulfuric acid/silica gel and 4 g of 33% 1 M sodium hydroxide/silica gel) and basic alumina column chromatography. Sample extracts were then fractionated at ambient pressure using a Michael-Miller type chromatographic column. The column was packed with 2 g of a 20:1 charcoal/silica gel adsorbent mixture and sequentially eluted with 60 ml of 1:4 methylene chloride : cyclohexane, 40 ml of 1:9 methylene chloride : toluene and 25 ml of toluene to isolate the di-, mono-, and non-*ortho* PCB congeners in fractions 1, 2 and 3, respectively. The fraction containing the PCDD/PCDF was then recovered by reversing the column and eluting with 200 ml toluene All four fractions collected from the charcoal column were then analyzed individually by high resolution mass spectrometry using a VG Autospec Ultima (VG Analytical, Manchester ,U.K.) double focusing instrument working at >10,000 resolving power (10% valley) operated in electron impact mode (EI) at 36eV coupled to a HP-5890 SeriesII gas chromatograph (Hewlett-Packard, Wilmington, Delaware, U.S.A.) equipped with a 60 m x 0.25 mm id. DB-5MS fused silica capillary column (J&W Scientific, Folsom, California, U.S.A).

Results and Discussion

The geographical distribution of HAHs in the Galveston Bay is heavily dominated by the intense urban and industrial activity located along Buffalo Bayou in the upper portion of the Houston Ship Channel.[9] In general, a concentration gradient is observed for most of the contaminants as sampling stations progress seaward and away from the upper portion of the bay. The concentrations and distributions of the analytes targeted in this study are presented in Table 1 and 2. Total PCDD/PCDF expressed as the sum of all the 2,3,7,8-substituted isomers was much higher in the abiotic compartments than in any of the organisms analyzed. Sediment distributions were mainly comprised of the heavier, highly chlorinated PCDDD/PCDF isomers (i.e. OCDD). Nevertheless, 2,3,7,8-TCDD and TCDF were detected in most sediment samples at concentrations ranging from non detected (nd.) to 4.44 pg/g and 0.650 to 7.46 pg/g respectively. In contrast, these two isomers are much more concentrated in the tissues of the analyzed organisms. 2.3,7,8-TCDD concentrations ranged from 1.15 to 16.4 pg/g in the American oysters, 1.10 to 138 pg/g in the Blue crabs and 11.1 to 101 pg/g in the Catfish livers while 2,3,7,8-TCDF concentrations were between 2.31 and 50.6 pg/g in the American oysters, from 5.77 to 385 pg/g in the Blue crabs and 5.57 to 8.04 pg/g in the Catfish livers. Although these congeners appear to be highly concentrated by the organisms, OCDD was still detected in most of the species at concentrations ranging from 12.5 to 172 pg/g. Among species, Blue crabs contained the highest concentrations of the lower molecular weight PCDD/Fs when compared with the oysters

and the catfish livers. The PCB distribution was dominated by the presence of congeners 138, 118, and 105 and to a minor extent 128,158,156, 170 and 77. However, in the Ship Channel organisms all targeted PCB congeners were detected including some which are only found at very low concentrations in Aroclor mixtures such as PCB 114, 123, and 167. Although extensive bioaccumulation was observed for all species, contrary to the trend noticed for the PCDD/PCDFs the concentrations of the toxic PCB congeners in the catfish livers were much more elevated than in the crabs and oysters. In order to simplify the interpretation of the data, the 2,3,7,8-TCDD toxic equivalents (TEQs) were calculated using the available toxicity equivalency factors (TEF).[5] However, for those PCB congeners where no TEF was available a more conservative approach was used and the value for a representative congener was used (i.e the TEF for PCB 77 was used for PCB 81). TEQs concentrations varied as follows: levels between 8.68 to 50.6 pg/g were observed for oyster samples, between 13.9 and 422 pg/g for the Blue crab tissues, and between 44.4 to 424 pg/g for the Catfish livers. In contrast, the TEQs observed for the sediments ranged from 2.04 to 10.12 pg/g. While there is a clear increasing trend for TEQ concentrations between organisms from the lower bay and the Ship Channel, the sediment TEQs does not show a significant trend. The individual contributions of the HAHs to the TEQ for all samples analyzed from Todd's Dump, a station located in the middle of Galveston Bay, are shown in Figure 2. The graphs indicate that the major contribution to the TEQ for the sediments is due to the presence of high molecular weight PCDD/PCDFs. However, the non-ortho PCB congeners appear to play a major role in the TEQs observed for the biological samples (29 to 74%). In addition, in spite of their relatively high concentrations, the di-ortho PCB congeners have a very limited or negligible contribution to the observed TEQs (<2%).

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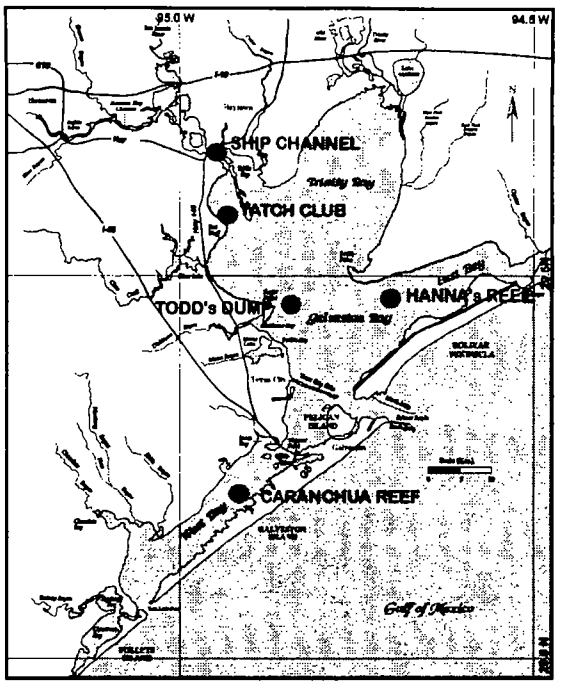

Figure 1 - Sampling sites along the Galveston Bay System.

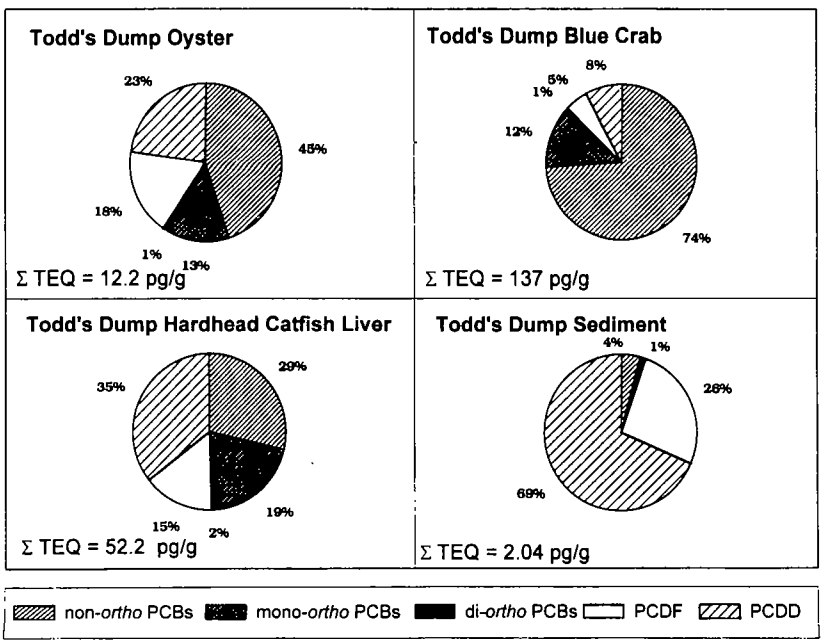

Figure 2.- Percentage contribution of non-, mono, -di-ortho PCB congeners; PCDF and PCDD to the 2,3,7,8-TCDD Toxic Equivalents (TEQs) in samples from the Todd's Dump site.

Table 1.- Concentrations (pg/g) of the seventeen 2,3,7,8-substituted PCDD/PCDF in selected organisms and sediments from Galveston Bay, Texas.

	2378-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	Total PCDD/F
Oysters																		
Caranchua Reef	2 31	(3.65)	(3 25)	nd.	(4.86)	5.47	5.96	nd.	nd.	nd.	1.98	nd.	nd.	nd	nd.	10.7	51.54	89.7
Hanna's Reef	2.40	(2.42)	nd.	nd.	(1.89)	(1.88)	(3.70)	nd.	nd.	nd	1.15	(2.43)	(3.20)	(3.30)	(2.91)	12.0	122	159
Todd's Dump	8.08	(1.31)	(1.46)	nd	(1.43)	(1 37)	(3.52)	nd.	nd.	(2.24)	1.56	(1.72)	(2.41)	nd.	nd.	8.90	47.5	81.5
Yatch Club	21.7	(2.03)	(3.02)	nd.	nd.	nd.	nd.	nd.	nd.	nd.	7.83	(2.72)	(2.63)	(3.87)	(2.57)	12.7	121	180
Ship Channel	50.6	(2.46)	(3.03)	nd.	(1.93)	(2.21)	(3.15)	(3 59)	nd.	(8.38)	16.4	(2.75)	(2.97)	(3 80)	(2.00)	17 5	172	293
Blue Crabs																		
Caranchua Reef	5.77	nd.	(3.12)	(1.01)	(1.61)	(1.36)	(2.36)	(2.12)	nd.	nd.	1.10	(4.07)	(2.37)	(2.41)	(2.42)	7.19	12 5	49.4
Hanna's Reef	10.9	(1.73)	(4.59)	(0.81)	(1.15)	(1.18)	(1 16)	(1.55)	nd.	nd.	2.06	(4.71)	5.26	7.00	5.80	11.7	24.2	83.8
Todd's Dump	28.9	(2.78)	6.25	(2.16)	(1.86)	(1.71)	(1.49)	(1.99)	nd.	nd	6.92	(4.33)	5.81	5.51	(3.51)	12.3	27.7	113
Yatch Club	124	5.65	14.5	(2.68)	(2.39)	(2.23)	(2.35)	(3.29)	nd.	nd.	43.4	7 98	(4.03)	8.74	4.07	12.0	32.6	270
Ship Channel	385	8.44	17.9	5 07	(3.21)	(2 19)	(2.08)	5.84	nd.	nd.	138	7.93	6 07	8 69	4.04	11.7	31.1	637
Hardhead Catfish Livers																		
Caranchua Reef	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hanna's Reef	5.57	(4.17)	(6.23)	nd.	(3.90)	(2.58)	(9.57)	(4.45)	nd.	nd	11.1	15.3	(7.42)	12.3	nd.	31.6	50.4	165
Todd's Dump	5.69	(6 27)	(4.84)	(5.73)	(6.98)	(7.92)	19.3	12.5	(6.72)	(16.14)	10.7	11.5	(9.12)	(8.09)	nd.	25.9	50.3	208
Yatch Club	8.46	18.4	nd.	10 3	16.0	nd.	50 5	nd.	nd.	nd.	15 0	17.9	18.4	15.6	nd.	39.0	109	318
Ship Channel	8.04	(8.32)	16.2	nd.	nd.	nd.	nd.	nd	nd.	nd.	101	15.0	nd.	13.6	nd.	53.1	133	348
Sediments																		
Caranchua Reef	0.650	(0.410)	(0.400)	(0.640)	(0 510)	(0.510)	(0.430)	5.74	(0.610)	19.8	(0 160)	(0.760)	(1.37)	2.16	5.03	62.7	632	734
Hanna's Reef	1.26	(0.340)	(0.250)	(0.760)	(0.360)	(0.440)	(0.250)	5.14	(0 410)	10.4	(0.380)	(0.950)	2.07	3.01	8.05	120	2314	2468
Todd's Dump	0.703	(0.215)	(0.583)	(0.453)	(0.280)	(0.318)	(0.208)	2.44	(0.190)	(4.94)	(0.200)	(0.218)	(0 398)	(0.710)	(1.45)	27.2	551	592
Yatch Club	1.38	(0.225)	(0.339)	(0.407)	(0.328)	(0.324)	(0.174)	3.50	(0.291)	14.7	0.585	(0.266)	(0.497)	(0.764)	(1.34)	29.5	725	780
Ship Channel	7.46	(0.720)	(0.780)	(1.76)	(0.820)	(0.770)	(0.240)	2.08	2 09	101	4.44	(0 420)	(0.860)	2.05	3 09	66.6	1176	1371

na.: not analized
nd.: non detected

mi.: matrix interference
(0.355): the number is below the method determination limit.

Table 2.- Concentrations (pg/g) of non-, mono- and di-ortho PCB congeners in selected organisms and sediments from Galveston Bay, Texas.

	non-ortho congeners				mono- ortho congeners								di-ortho congeners				
	PCB 77	PCB 81	PCB 126	PCB 169	PCB 105	PCB 114	PCB 118	PCB 123	PCB 156	PCB 157	PCB 167	PCB 189	PCB 128	PCB 138	PCB 158	PCB 166	PCB 170
Oysters																	
Caranchua Reef	227	11.2	9.31	(0.542)	376	nd	1800	34.6	180	38.8	100	nd.	345	2705	277	(8.18)	436
Hanna's Reef	133	6.85	15.4	(2.90)	564	nd.	2217	28.9	212	59.1	194	39.0	608	3986	181	nd.	475
Todd's Dump	278	11.5	23.4	(3.76)	910	103	5631	76.4	304	68.6	196	(14.5)	859	5980	137	(8.71)	410
Yatch Club	537	17.5	31.1	mi.	-	-	-	-	-	-	-	-	-	-	-	-	-
Ship Channel	831	29.4	81.7	7.58	4099	459	21185	328	1075	282	769	89.1	3377	22514	nd.	52.0	1211
Blue Crabs																	
Caranchua Reef	219	16.3	30.1	(4.61)	972	35.5	3770	71.7	239	73.5	214	38.6	579	3753	229	(12.1)	597
Hanna's Reef	275	16.8	56.1	13.1	2277	109	9863	192	840	263	503	114	2423	14276	797	(19.4)	2503
Todd's Dump	4274	216	539	42.6	10410	532	54002	595	3871	1010	2671	117	7800	55875	4348	180	9505
Yatch Club	2492	168	395	39.3	21507	1365	110218	1396	10681	2389	6060	1138	17650	156076	13965	488	16501
Ship Channel	8637	476	594	37.8	50245	2607	189700	2914	12579	1234	7318	1266	26207	178917	19138	449	15959
Hardhead Catfish Livers																	
Caranchua Reef	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hanna's Reef	294	36.1	127	35.8	-	-	-	-	-	-	-	-	-	-	-	-	-
Todd's Dump	450	50.2	98.6	(3.48)	6027	410	32452	562	2944	902	1584	564	6638	41738	3566	136	7923
Yatch Club	1059	111	82.5	19.7	4447	148	18137	561	2610	871	1004	250	6586	42679	2575	115	10159
Ship Channel	680	123	940	55.9	124969	7136	528823	6239	33347	9150	13911	2850	81959	538767	46599	1480	69586
Sediments																	
Caranchua Reef	10.3	na.	nd.	nd.	-	-	-	-	-	-	-	-	-	-	-	-	-
Hanna's Reef	8.17	na.	nd.	nd.	-	-	-	-	-	-	-	-	-	-	-	-	-
Todd's Dump	5.06	(0.403)	(0.345)	nd.	18.5	(0.941)	54.4	(0.841)	(8.46)	nd.	(3.36)	(1.72)	16.8	84.40	12.50	nd.	38.50
Yatch Club	10.7	(0.537)	(0.613)	(0.268)	32.8	(1.80)	94.4	(1.77)	14.70	(3.01)	(6.14)	(1.82)	28.2	137.00	16.20	(0.547)	79.20
Ship Channel	92.3	na.	4.07	(0.530)	-	-	-	-	-	-	-	-	-	-	-	-	-

na.: not analized
nd.: non detected

mi.: matrix interference
(0.355): the number is below the method determination limit.

PCB 77 : 3.3',4,4'- TCB
PCB 81 : 3,4,4',5'- TCB
PCB 126 : 3,3',4.4',5- PeCB
PCB 169 : 3,3',4.4',5.5'- HxCB

PCB 105 : 2,3,3',4.4'- PeCB
PCB 114 : 2,3,4,4',5- PeCB
PCB 118 : 2,3',4.4',5- PeCB
PCB 123 : 2'.3,4,4',5- PeCB
PCB 156 : 2,3,3',4.4',5-HxCB
PCB 157 : 2,3,3',4.4',5'-HxCB
PCB 167 : 2.3.4,4',5,5'-HxCB
PCB 189 : 2,3,3'.4.4',5,5'-HpCB

PCB 128 : 2,2',3,3',4,4'-HxCB
PCB 138 : 2.2',3,4,4',5-HxCB
PCB 158 : 2,3,3',4,4',6-HxCB
PCB 166 : 2.3.4,4',5,6-HxCB
PCB 170 : 2.2',3,3',4,4'.5-HpCB