Associations between Dioxins/Furans and Dioxin-Like PCBs in Sediment and Blue Crab in Anthropogenically Impacted Estuaries

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Introduction

Dioxin/furan compounds (PCDD/Fs) are ubiquitous environmental contaminants that are very stable to chemical and microbiological degradation and therefore persistent in the environment. PCDD/Fs are fat-soluble and thus tend to bioaccumulate in the lipids of animal tissues as they age, and in the food chain. Food contaminated by environmental PCDD/Fs is the major source for human exposure to PCDD/Fs. Out of 210 congeners of PCDD/Fs 17 individual congeners exhibit toxicity. 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. They are persistent organic pollutants due to their toxicity and stable structure, and biomagnify as they move up through the food chain.

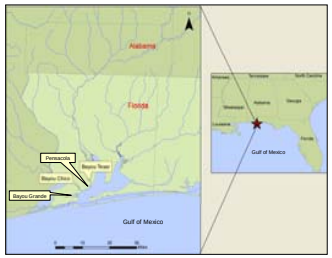
PCDD/Fs and DL PCBs are very stable in soils and aquatic sediments, especially those rich in organic matter. Consequently, these media act as a reservoir for the PCDD/Fs and DL PCBs. In aquatic environments, bottom dwelling organisms such as crabs provide a pathway for the transfer of the PCDD/Fs and DL PCBs from the sediments to humans via the foodchain.

Objectives

The objective of our study was to help remedy the incomplete knowledge of the relationships between PCDD/Fs and DL PCBs in sediments and biota by evaluating the connections between the quantity, toxicity, and compositional profile of PCDD/Fs and DL PCBs in the blue crab (*Callinectes sapidus*) and sediments in three anthropogenically altered estuaries.

Study Area

The three estuaries that were sampled for this study are part of the Pensacola Bay System and are located in Northwest Florida (Figure 1, below). 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.



Methods

- Composite sediment samples were collected at 17 sites in Bayou Chico, 13 in Bayou Texar, and 23 in Bayou Grande.
- Crabs were collected with commercial traps that were deployed for two to three days. Only male crabs over 10.2 cm in width were retained. Seven to 15 crabs were composited for each sampling location.
- Analyses: HRGC-HRMS using USEPA method 1668A for DL PCBs, 1613B for PCDD/Fs in sediments, and 8290B for PCDD/Fs in crab tissue.
- Total Toxic Equivalents (TEQ) were calculated with WHO (2005) TEF values for humans/mammals. Half the detection limit was substituted for analytical results below the detection limit. 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.

Data Summary

Table 1. Geomean of PCDD/F and DL PCB concentrations and TEQ [ng/kg] for sediments and crab samples.

	Total PCDD/F	TEQ PCDD/F	Total DL-PCB	TEQ DL-PCB	TEQ Total
			Bayou Grande (geomean)		
sediment	797.1	2.57	783.0	1.20	5.04
HP*	45.80	4.18	21090	13.73	19.03
muscle	1.70	0.15	492.6	0.39	0.56
			Bayou Chico (geomean)		
sediment	5207	15.81	1186	0.79	18.41
HP*	161.0	13.43	35923	10.04	23.54
muscle	9.44	0.36	670.8	0.18	0.54
			Bayou Texar (geomean)		
sediment	823.0	2.29	584.3	0.29	2.67
HP*	38.61	5.05	31066	9.48	14.94
muscle	1.03	0.12	578.6	0.18	0.30

*HP = hepatopancreas

Mass Concentrations

PCDD/F mass concentrations in crab samples are much lower than in sediments (Table 1, above) but mirror the trend observed in sediments (highest in Bayou Chico, lower but comparable in Bayous Grande and Texar). DL PCBs concentrations are much higher in crabs but also display the same trend. Similarity of trends and correlation (Figure 2, below) point to sediments as a major direct or indirect source of PCDD/Fs and DL PCBs for crabs.

Table 2. Spearman correlation between mass concentrations in crab samples and two nearest sediment samples.

	PCDD/F	DL PCB
Crab muscle	0.83	0.64
Crab HP	0.74	0.43

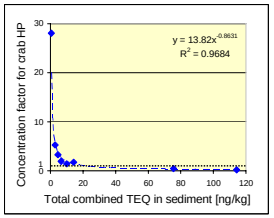
TEQ

The PCDD/F TEQ is higher in HP than in the respective sediments but again mirrors the levels in the sediments (Table 1, above). As shown above, total PCDD/F mass concentrations are lower in HP than in sediments, and thus the higher TEQ indicates greater bioaccumulation of high TEF than of low TEF PCDD/Fs in blue crab HP. Total combined TEQ is also higher in the HP than in the sediments of the respective estuaries. This is in part due to the preferential accumulation by blue crab HP of PCDD/Fs with high TEF values but also to the much higher mass concentrations of DL PCBs in HP (Table 1).

Table 3. Spearman correlation between total combined TEQ in crab samples and two nearest sediment samples.

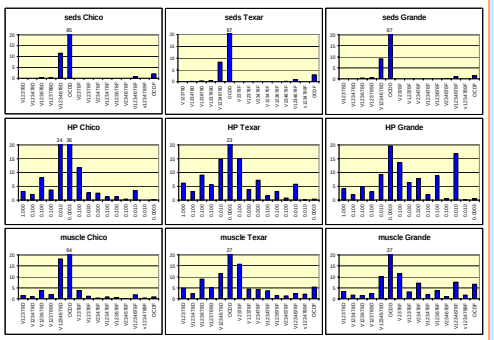
	Total combined TEQ
Crab muscle	0.90
Crab HP	0.52

Figure 2. A relative upper limit exists for how much total combined TEQ can accumulate in crab HP from sediments via the multiple processes involved. 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.



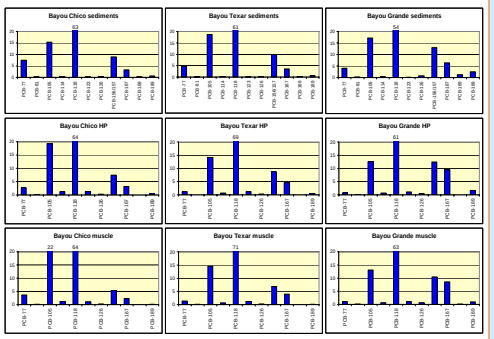
Congener Profiles

Figure 3. 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.



The PCDD/F congeners for the crab samples are more evenly distributed than those for the sediments (Figure 3, above). This indicates that the crabs do not bioaccumulate the various PCDD/F congeners in the proportion that they are present in the sediment. 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. This corroborates the before made contention that congeners with higher TEFs preferentially bioaccumulate in the HP, and thus the HP has a higher PCDD/F TEQ per unit mass concentration than the sediments.

Figure 4. Average DL PCB profiles for sediments, HP, and muscle in the three estuaries. Relative proportion on Y axis is in %.



The DL PCB profiles in crabs are similar to those for the sediments. They are more similar to those for the sediments than the PCDD/F profiles in crabs. This can be explained by the higher accumulation efficiencies of DL PCBs compared to PCDD/Fs.

Acknowledgements

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Congener Profiles - PCA

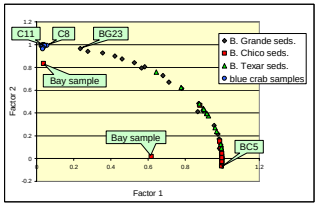


Figure 5. PCA loadings plot for PCDD/Fs and DL PCBs.

Figure 5 (above): Sediments from the three estuaries have different congener profiles but some overlap exists, which can be explained by the presence of both regional and local sources of PCDD/Fs and DL PCBs. Crab samples are clustered and 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 shift the original congener profiles of the sediments.

Figure 6 (to the right): Comparison of the average profiles for sediments, HP and muscle suggests that the crab-sediment separation in the loadings plot (Figure 5, above) is due to a higher proportion of DL PCBs in the crab samples.

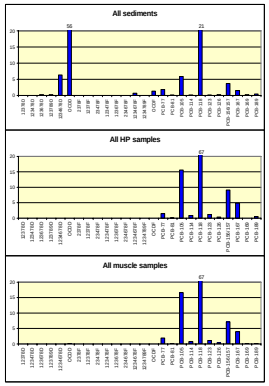
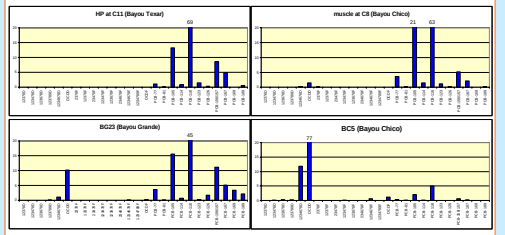


Figure 7 (below): Comparison of profiles for individual samples from various parts of the loadings plot (Figure 5) indicates that the processes involved in bioaccumulation in blue crab are also selective for PCDD/Fs versus DL PCBs.



Conclusions

- Compared to sediment profiles, more lesser-chlorinated PCDD/Fs that have higher TEFs accumulate in crab HP.
- TEQs in crabs correlate well with the local TEQs in sediments, suggesting that an association exists between the TEQ in sediments and in blue crab.
- Augmentation of total combined TEQ in crab HP is limited and does not continue to increase with increasing TEQ in sediment.
- Congener profiles in the crab samples are distinct from those in the sediments, regardless of the specific congener composition of the sediments.