CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN SEAFOOD PRODUCTS FROM THE U.S. RETAIL MARKET

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Abstract
Measurable levels of persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), in aquatic organisms are relatively well documented and recent studies have suggested that shrimp may contain higher concentrations of these chemicals than other types of aquatic food products. In this study, we measured concentrations of the 209 PCB congeners in 87 samples of wild-caught and farm-raised shrimp and three samples of wild-caught crab from various countries around the world. No significant differences in PCB concentrations were observed between wild-caught and farm-raised shrimp. However, concentrations of PCBs differed significantly ($p<.0001$) among countries of origin. Lowest and highest median concentrations of PCBs were observed in shrimp originating in Bangladesh and Belize, respectively. Differences in PCB concentrations observed among shrimp from varying geographic regions implies the source of PCB exposure could be related to regional contamination. Regardless, the PCB concentrations measured in this study are well below government-established tolerance levels for PCBs in edible food.

Introduction
Polychlorinated biphenyls (PCBs) were commonly used in a variety of applications including lubricants, paint stabilizers, polymers and adhesives, varnishes, waxes, resins, coatings, and fluids for heat transfer and hydraulics.[1] Since PCBs persist in the environment and readily bioaccumulate in fatty tissue, the U.S. Environmental Protection Agency (EPA) banned their manufacture in 1977.[2] While the storage, transport, and disposal of PCB-containing materials has been strictly regulated, prevalent use of these compounds over time has contributed to their widespread distribution throughout the environment.

For humans, fish consumption has been classified as a primary route of PCB exposure.[3,4] Several recent studies have measured PCB concentrations in a number of aquatic food sources including catfish, char, crab, salmon, tilapia, trout, mussels, oysters, squid, clams, and shrimp.[5-9] One recent study reported levels of PCBs in shrimp as three times higher than those observed in mussels and oysters.[10] It is estimated that over four million tons of shrimp are consumed per year worldwide.[11] The United States is, reportedly, the largest world market for shrimp imports with U.S. annual consumption of shrimp per capita reaching ~3.7 pounds in 2002.[11] Other major markets for shrimp imports include Japan, France, the United Kingdom, Spain, and Italy.

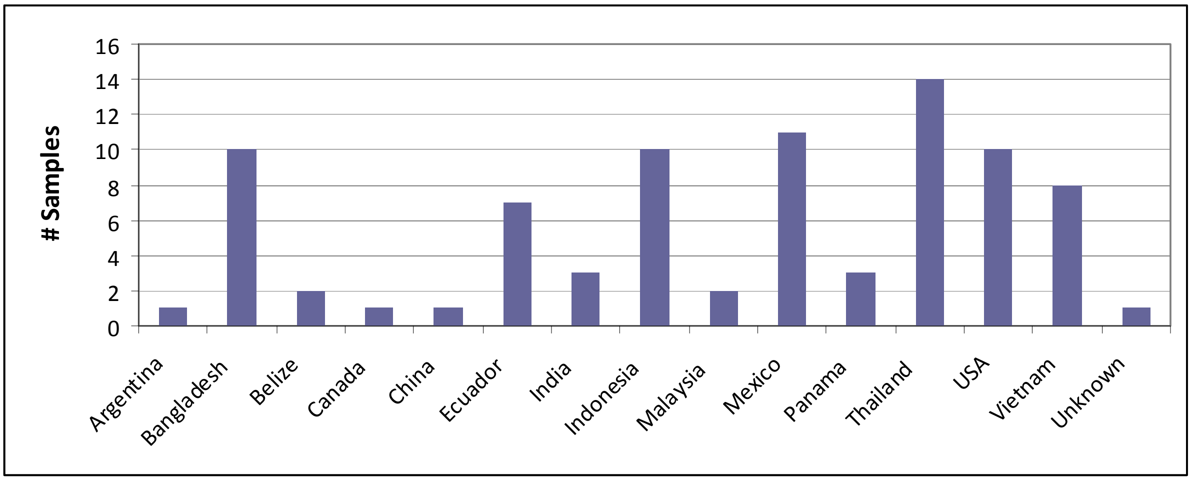
Approximately 70-80% of shrimp imported to the U.S. is farm-raised from tropical regions in Asia and Latin America.[12] Thailand accounts for 25% of the world's shrimp production, followed by China (14%), Indonesia (12%), and Ecuador (10%).[13] Commercial feeds such as those frequently used in shrimp farms may contain background levels of PCBs and other contaminants and are thought to contribute to the chemical loads measured in shrimp food products. In the present study, we quantified PCB levels for all 209 congeners from both wild-caught and farm-raised shrimp (cooked and uncooked) and wild-caught crab from 14 countries in order to assess PCB loading.

Materials and Methods
Eighty-four raw shrimp samples, three cooked shrimp samples, and three raw crab samples were randomly purchased from local fish markets, supermarkets, and grocery stores in the San Francisco and Sacramento areas in Northern California between February and April 2009. Wild-caught shrimp samples originated from Argentina, Bangladesh, Mexico, Panama, Thailand, USA, and Vietnam while farm-raised shrimp samples originated from Bangladesh, Belize, Canada, Ecuador, India, Indonesia, Malaysia, Mexico, Thailand, USA, and Vietnam. The breakdown of uncooked shrimp samples by country is given in Figure 1. One farm-raised shrimp sample was from an unknown country of origin and one sample each from Bangladesh, Mexico, and Thailand

were not identified as wild-caught or farm-raised. The crab samples were wild-caught in the USA. Of all shrimp identified as wild-caught or farm-raised, 27% (n=23) were wild caught and 73% (n=61) were farm-raised.

After purchase, all samples were individually wrapped, labeled, and frozen on ice for shipment to the analytical laboratory. Samples were analyzed by Vista Analytical Laboratory (El Dorado Hills, CA) using high resolution gas chromatography-mass spectrometry according to the EPA Method 1668. The samples were analyzed for all 209 PCB congeners, although multiple PCBs co-eluted (Table 1) resulting in a total of 168 reported PCB congeners/congener pairs for each sample. Samples with non-detected concentrations were assumed to have a value equal to the LOD divided by the square root of two.

Figure 1: Number of samples per country of origin for uncooked shrimp



In addition to the estimation of total PCB concentrations (∑tPCB: all 168 congeners/congener pairs), summed PCB concentrations were also calculated for three subsets of congeners: 1) all congeners in which more than 50% of the samples had concentrations greater than the congener specific LOD (∑51 PCB), 2) the seven indicator congeners (∑7 PCB: PCBs 28, 52, 101, 106/118, 138/163/164, 153, and 180), and 3) the 12 congeners with dioxin-like activity (∑DLC PCB: PCBs 77, 81, 126, 169, 105, 114, 106/118, 123, 156, 157, 167, and 189).

The arithmetic mean, median, and 25th and 75th percentiles of ∑7 PCB concentrations were characterized by sample type (wild-caught or farm-raised) and country of origin. Differences between groups were examined using the Wilcoxon rank sum test for significance. Student's t-test and ANOVA were used to evaluate differences in the average percent contribution of individual congeners to ∑7 PCB concentrations for sample type and country of origin, respectively. All data management and analyses were completed using Microsoft Excel and SAS software (Cary, NC) using an alpha level of 0.05.

Table 1: PCB co-eluted congeners

4/10	20/21/33	48/75	84/92	95/98/102	128/162	139/149
5/8	24/27	52/69	85/116	106/118	132/161	146/165
7/9	41/64/71/72	56/60	87/117/125	107/109	133/142	158/160
12/13	42/59	61/70	88/91	108/112	134/143	182/187
16/32	43/49	76/66	90/101	111/115	138/163/164	196/203

Results and Discussion

As presented in Table 2, cooked shrimp had the highest average lipid content and uncooked crab had the lowest at 0.57 and 0.26%, respectively. Average lipid content did not vary between farm-raised and wild-caught samples of uncooked shrimp.

Table 2: Percent lipid content of 90 crab and shrimp samples

	N	Mean (95% CI)	Range
Uncooked Crab*	3	0.26 (0.00 - 0.53)	0.18 - 0.39
Uncooked Shrimp	84	0.44 (0.39 - 0.48)	0.10 - 0.90
Farm-raised	58	0.42 (0.36 - 0.47)	0.10 - 0.90
Wild-caught	23	0.48 (0.41 - 0.55)	0.15 - 0.78
Unknown	3	0.50 (0.31 - 0.68)	0.42 - 0.57
Cooked Shrimp**	3	0.57 (0.31 - 0.84)	0.46 - 0.66

*All samples are wild-caught
** All samples are farm-raised

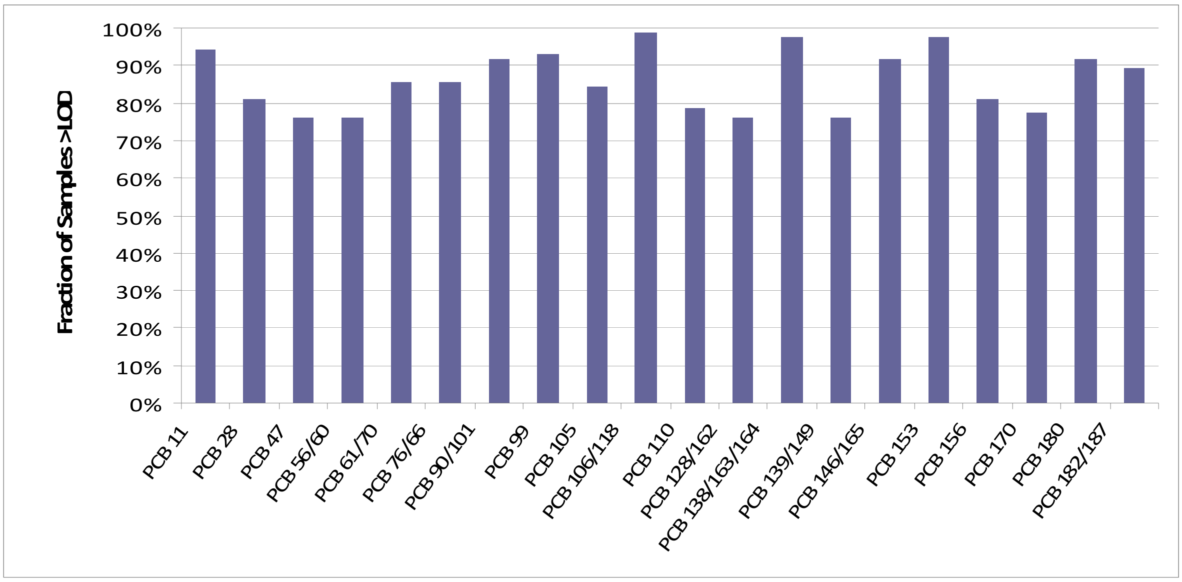
The median, range, and 95th percentiles of the four different summed PCB concentrations for uncooked crab, uncooked shrimp, and cooked shrimp are presented in Table 3. Median concentrations of PCBs ranged from 91 to 1083 pg/g wet weight for uncooked crab, 12 to 176 pg/g wet weight for uncooked shrimp, and 16 to 225 pg/g wet weight for cooked shrimp. Yet, among the three seafood groups sampled, the highest concentrations of PCBs were observed in uncooked shrimp with maximum total levels ranging from 193 to 2403 pg/g wet weight. The lowest concentrations were also observed in uncooked shrimp, suggesting wide variability of measured concentrations in this food product. In contrast, cooked shrimp samples had much less variability although median levels were, unexpectedly, higher than those for uncooked shrimp.

Table 3: PCB concentrations in uncooked crab and uncooked and cooked shrimp

		∑tPCB	**∑51 PCB**	**∑7 PCB**	**∑DLC PCB**
Uncooked crab	Median	1083.3	888	379.1	90.8
(n=3)	Range	(390.7-1617.9)	(284.3-1383.2)	(121.7-714.4)	(27.1-148.9)
	95%tile	1617.9	1383.2	714.4	148.9
Uncooked shrimp	Median	175.9	99.1	43.8	12
(n=84)	Range	(108.2-2403.3)	(26.8-2024.3)	(2.8-962.4)	(1.6-193.0)
	95%tile	1472.3	1075.2	474.8	99.6
Cooked shrimp	Median	225.4	143.1	65.1	15.8
(n=3)	Range	(171.2-249.8)	(89.0-168.6)	(39.3-85.4)	(12.9-18.0)
	95%tile	249.8	168.6	85.4	18

Twenty-three PCB congeners were not detected in any samples (PCBs 14, 23, 30, 34, 36, 46, 50, 54, 62, 65, 73, 80, 83, 89, 94, 96, 104, 127, 131, 145, 152, 186, and 192). Overall, the detection limits for this study were very low, with maximum levels ranging from 1.01 to 3.74 pg/g. Of the 168 congeners/congener pairs, 119 had a maximum LOD of one pg/g while only 21 had a maximum LOD between two and three pg/g and three congeners had maximum LODs greater than three pg/g. Figure 2 illustrates the fraction of uncooked shrimp samples with concentrations greater than the LOD for selected congeners.

Figure 2: Fraction of uncooked shrimp samples (n=84) with concentrations greater than the LOD for selected congeners



The distribution of ∑7 PCB concentrations in uncooked shrimp are shown by sample type (wild-caught and farm-raised) in Figure 3. Concentrations ranged from 8 to 600 pg/g wet weight for wild-caught shrimp and from 3 to 962 pg/g wet weight for farm-raised shrimp, with median values of 30 and 45 pg/g wet weight, respectively. Evaluation of ∑7 PCB concentrations by sample type demonstrated that levels were not statistically different between the two groups ($p=0.962$). These results were consistent with a study by Rawn et al. (2006) in which levels of PCBs in wild-caught samples were not significantly higher than farm-raised samples.[6]

For uncooked shrimp, ∑7 PCB concentrations varied significantly by country of origin ($p<.0001$). Figure 4 illustrates the quantitative differences among the different countries of origin in which five or more samples were collected. For this subset, shrimp from the USA had the highest concentrations with a median value of 114 pg/g wet weight. Interestingly, Mexico had the second highest concentrations but a much lower median level of 17 pg/g wet weight. This finding illustrates that the highest variability in PCB concentrations was observed in shrimp from two North American countries, both of which border the Gulf of Mexico where shrimping is a prominent industry. The lowest PCB concentrations were observed in samples from Bangladesh with a median value of 8 pg/g wet weight. Table 4 presents median, minimum and maximum ∑7 PCB concentrations from countries where three or less samples were collected. Of these, samples from Belize had the highest concentrations and the one sample from Argentina had the lowest.

The average percent contribution of each individual congener to ∑7 PCB for all uncooked shrimp is shown in Figure 5. As expected, PCBs 153 and 138/163/164 were the dominant congeners followed by PCB 106/118 and 90/101. For PCBs 28, 90/101, 106/118 and 153, the average percent contribution differed significantly between wild-caught and farm-raised shrimp ($p=0.016$, $p=0.021$, $p<0.001$, and $p<0.001$, respectively), with the average contribution for PCBs 28, 90/101, and 106/118 lower in wild-caught shrimp (data not shown). For PCB 153, the average percent contribution was significantly higher in wild-caught shrimp. With respect to country of origin, the average percent contribution of each congener, except for PCB 180, varied significantly among samples from Bangladesh, Ecuador, Indonesia, Mexico, Thailand, USA, and Vietnam (data not shown). Further analyses, such as principal component analysis and determination of homologue fractions, may help determine if these results could be attributed to PCB levels of feed or regional or local sources of contamination.

Figure 3: Distribution of ∑7 PCB concentrations measured in uncooked shrimp by sample type

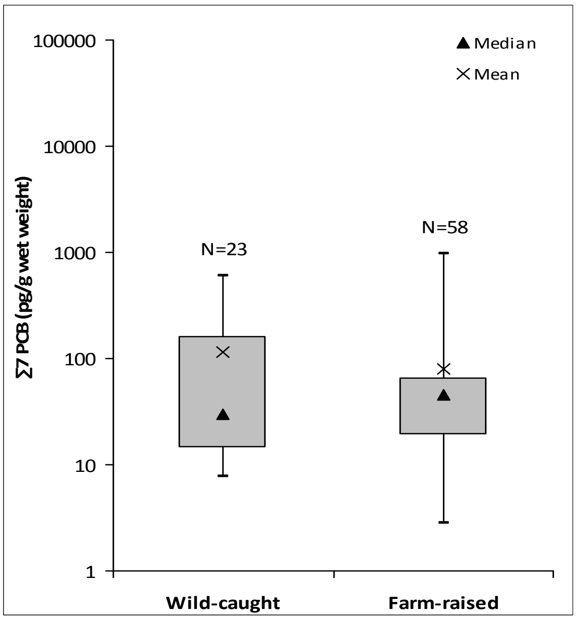


Figure 4: Distribution of ∑7 PCBs measured in uncooked shrimp by country of origin (>5 samples)

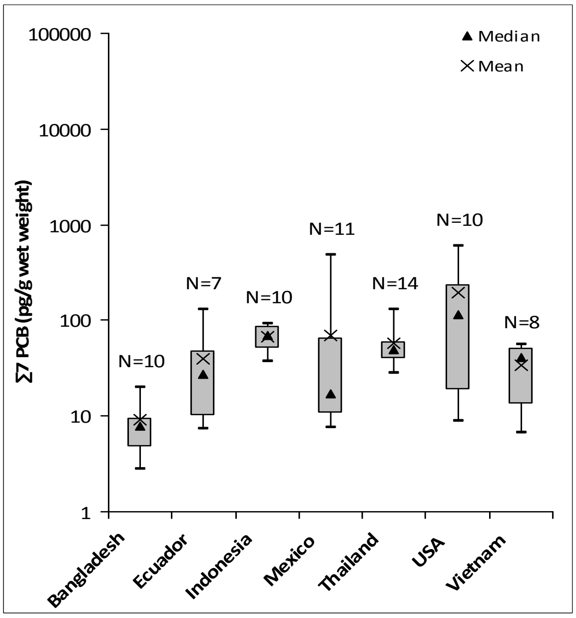
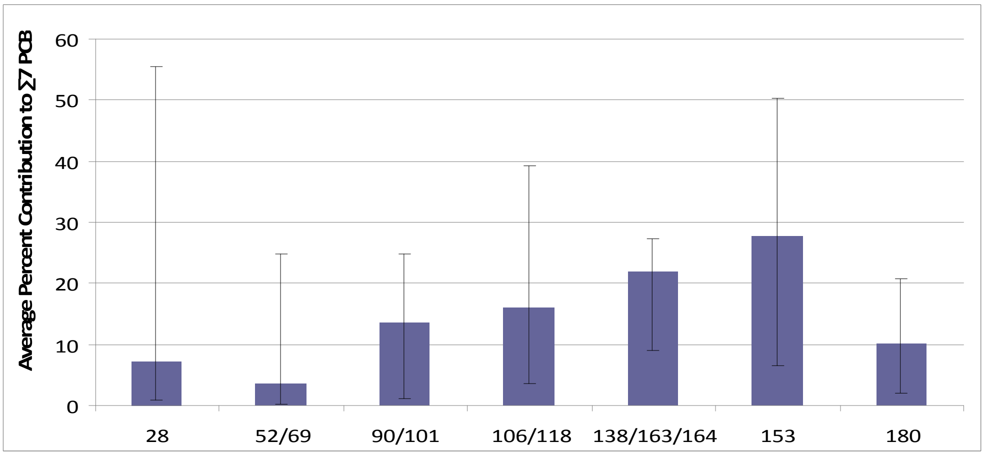


Table 4: ∑7 PCBs measured in uncooked shrimp by country of origin (≤ 3 samples)

Country	*N*	*Median*	*Range*
Argentina	1	12.6	-
Belize	2	935.3	908.3 - 962.4
Canada	1	30.0	-
China	1	121.9	-
India	3	27.4	20.2 – 39.6
Malaysia	2	71.9	43.4 – 100.4
Panama	3	53.4	29.9 - 163.1
Unknown	1	23.8	-

Figure 5: Percent contribution of congeners to ∑7 PCB for all uncooked shrimp (*N*=84)



Error bars represent the minimum and maximum

The range of levels measured in this study were similar to previously published levels in shrimp[6,8,9] while median levels were lower than median concentrations measured in other studies.[7] The highest PCB measures were obtained from shrimp collected in Belize, although we were able to acquire only two samples from this region. We observed no statistical difference in ∑7 PCB concentrations between wild-caught and farm-raised shrimp; however, we found a significant difference in ∑7 PCB levels among country of origin. Our results will be useful in determining intake and related cancer risk, which are expected to be very low, from consumption of PCBs in shrimp. Certainly, for all samples, levels of PCBs fell far below the U.S. Food and Drug Administration's tolerance level for these compounds in fish (two parts per million).[14] Our results provide valuable information concerning highly variable levels of PCBs in shrimp from some of the largest shrimp exporting regions in the world.

Acknowledgements
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