

# MEASUREMENTS OF PCDD AND PCDF CONCENTRATIONS IN WILD-CAUGHT AND FARM-RAISED SHRIMP FROM THE U.S. RETAIL MARKET

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## Introduction

Numerous studies have demonstrated that exposure to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) occurs through a number of different pathways.<sup>1,2</sup> For humans, consumption of meat, fish, and dairy are the primary routes of exposure and account for well over 90% of the daily intake of PCDD/Fs for the majority of the population.<sup>3</sup> Since an estimated four million tons of shrimp are consumed annually worldwide,<sup>4</sup> this food source may represent a significant contribution to the dietary intake of these compounds for populations that consume shrimp as a principal food source.

To characterize levels of persistent organic compounds in seafood from the U.S. retail market, we collected 84 samples of both wild-caught and farm-raised shrimp (warm-water, uncooked) between February and April 2009. The shrimp originated from 14 countries in three continents. We previously reported that PCB concentrations were not significantly different between farm-raised and wild-caught shrimp, but that concentrations varied significantly among shrimp from different countries.<sup>5,6</sup> Additionally, several shrimp samples from North American countries had higher PCB concentrations than expected.<sup>7</sup> In this study, we extended our analysis to include the 17 laterally-substituted PCDD/Fs, comparing concentrations of these compounds in farm-raised to wild-caught samples. A comparison of the highest measured levels in shrimp from different countries of origin is also presented.

## Materials and Methods

Sample collection has been described in detail elsewhere.<sup>5,6</sup> To summarize, 84 uncooked warm-water shrimp were obtained from identified fish markets, grocery stores, and supermarkets throughout Northern California between February and April 2009. Twenty-seven percent were wild-caught (n=23), 69% were farm-raised (n=58), and 4% (n=3) could not be identified as wild-caught or farm-raised. The shrimp originated from 14 countries in three continents: 57% (n=48) were from Asia, 32% (n=27) were from North America, 10% (n=8) were from South America and 1% (n=1) was from an unknown country of origin.

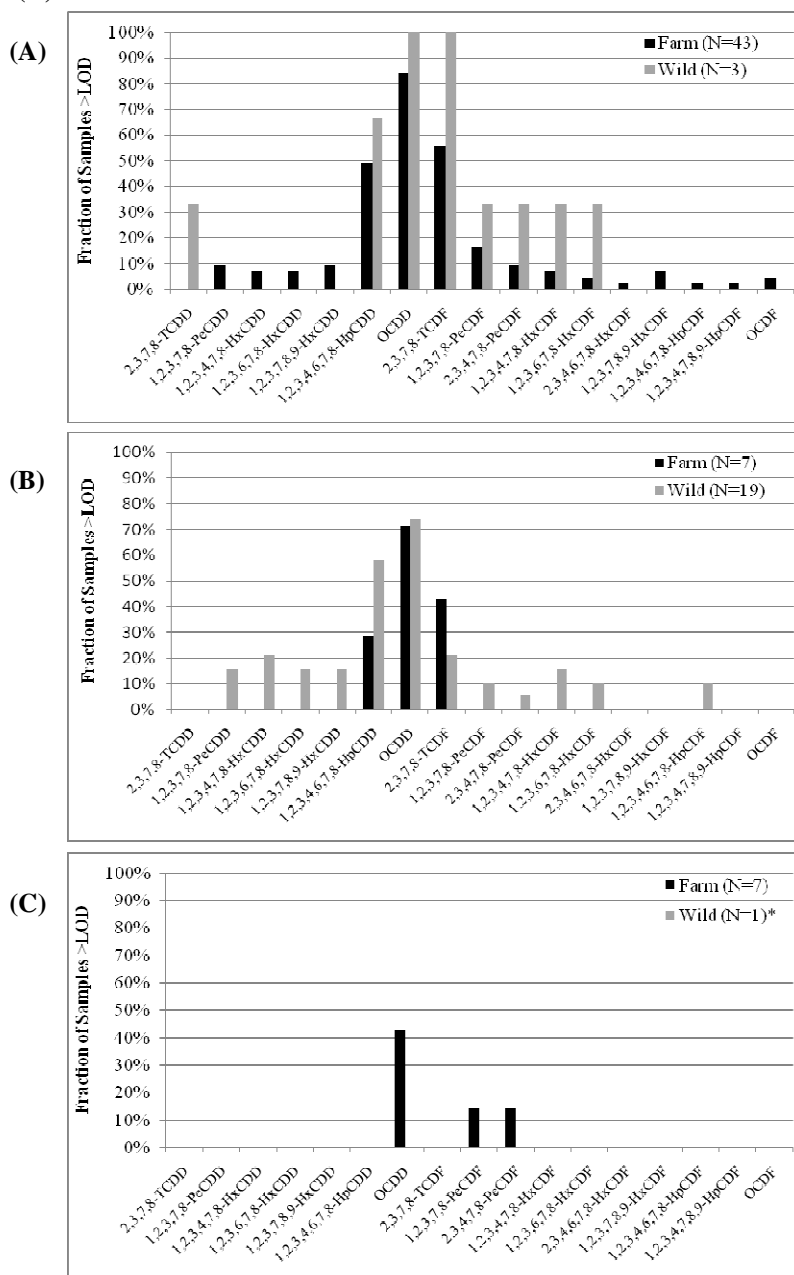
Samples were analyzed by Vista Analytical Laboratory (El Dorado Hills, CA) for the 17 laterally-substituted PCDD/F congeners using high-resolution gas chromatography-mass spectrometry according to the EPA Method 1613. The arithmetic mean, median, and 95<sup>th</sup> percentile of total wet weight concentrations of detected PCDD/F congeners were characterized by sample type. Differences between/among groups were examined using the Wilcoxon rank-sum test for significance and an alpha level of 0.05. All data analyses were conducted using Microsoft Excel and SAS software (Cary, NC).

## Results and Discussion

Overall, detection limits for this study were very low, with maximum limits ranging from 0.04 to 0.32 pg/g. Nineteen percent (n=16) of all shrimp samples had no detected PCDD/Fs, 60% (n=50) had between one and three detected congeners, 17% (n=14) had between four and seven detected congeners, and 4% (n=4) had eight or more detected congeners. Both farm-raised and wild-caught shrimp had an average of only two detected congeners each, and the average number of detected congeners did not vary between these two groups (p=0.461). As shown in Figure 1, numerous PCDD/F congeners were detected in Asian and North American samples that were absent from the South American samples. Limits of detection for the PCDD/F congeners were somewhat elevated in the South American samples relative to the North American and Asian samples, but not to a degree sufficient to account for the greater number of non-detected PCDD/F congeners in the South American shrimp.

OCDD was the predominant congener detected in shrimp from all three continents (Figure 1), which is similar to PCDD/F congener profiles previously reported in cephalopods and shellfish from Spain.<sup>8</sup> TCDF and HpCDD were also prevalent in the samples from Asia and North America. TCDD was detected in only one sample: a wild caught shrimp from Asia. Interestingly, the Asian farm-raised samples contained a greater variety of detected congeners relative to the wild samples, yet the reverse was true for the North American samples. Also, penta- and hexa-CDDs were detected in farm-raised Asian samples, but not in farm-raised North American samples, whereas penta- and hexa-CDDs were detected in wild-caught North American samples, but not in wild-caught Asian samples. The single wild-caught sample from South America had no detected PCDD/F congeners.

**Figure 1: Fraction of shrimp samples with detected PCDD/F concentrations for (A) Asia, (B) North America, and (C) South America**



The median, range, and 95<sup>th</sup> percentile wet weight concentrations for detected PCDD/F congeners are presented in Table 1. Median concentrations for most congeners were similar between sample types and ranged from 0.01 to 0.20 pg/g for wild-caught shrimp and 0.02 to 0.16 pg/g for farm-raised shrimp. The median concentration of HpCDD differed by sample type and was four times higher in wild-caught compared to farm-raised shrimp. The maximum level of HpCDD in farmed shrimp, measured in a sample from Asia, was twice as high as the maximum level in wild shrimp, measured in a sample from North America. Additionally, the maximum level of TCDF was considerably greater in the farm-raised group (5.11 pg/g) compared to the wild-caught group (0.28 pg/g). Concentrations of OCDD were highest for both sample types with maximum levels of 2.15 and 5.84 pg/g in wild-caught and farm-raised shrimp, respectively.

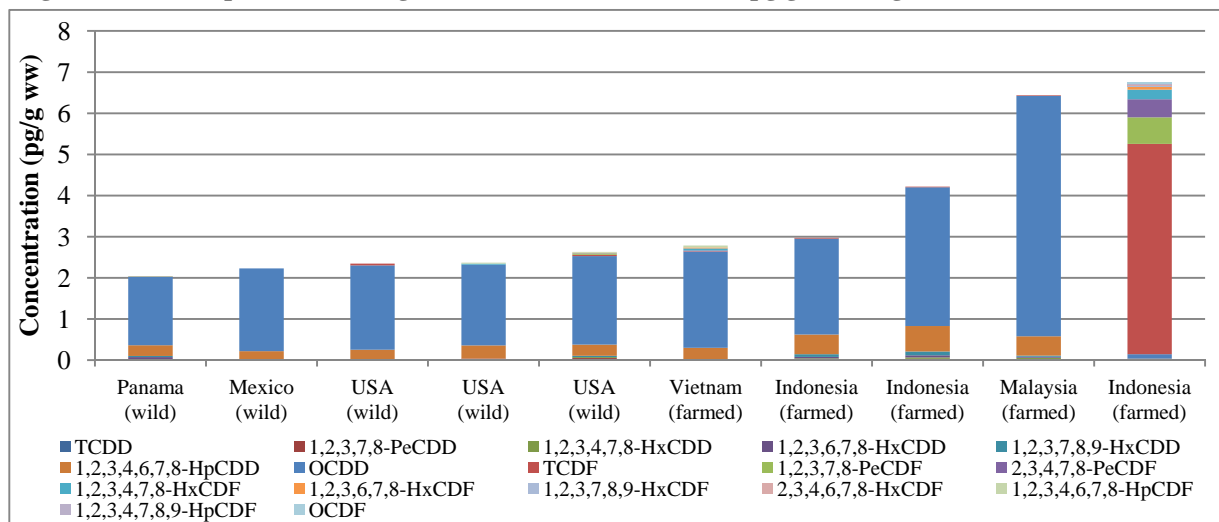
**Table 1: Summary statistics (pg/g wet weight) for detected PCDD/Fs in shrimp by sample type**

	Wild-Caught				Farm-Raised			
	N	Range	Median	95%ile	N	Range	Median	95%ile
2,3,7,8-TCDD	1	--	0.01	--	0	--	--	--
1,2,3,7,8-PeCDD	3	0.04-0.06	0.05	0.05	4	0.02-0.07	0.03	0.07
1,2,3,4,7,8-HxCDD	4	0.02-0.03	0.03	0.03	3	0.02-0.03	0.03	0.03
1,2,3,6,7,8-HxCDD	3	0.046-0.05	0.05	0.05	3	0.02-0.05	0.04	0.05
1,2,3,7,8,9-HxCDD	3	0.03-0.04	0.03	0.04	4	0.02-0.09	0.05	0.09
1,2,3,4,6,7,8-HpCDD	13	0.02-0.32	0.17	0.32	23	0.01-0.62	0.04	0.47
OCDD	17	0.05-2.15	0.20	2.15	45	0.06-5.84	0.16	2.33
2,3,7,8-TCDF	7	0.02-0.28	0.04	0.28	28	0.01-5.11	0.03	0.30
1,2,3,7,8-PeCDF	3	0.02-0.06	0.04	0.06	8	0.02-0.64	0.05	0.64
2,3,4,7,8-PeCDF	2	0.02-0.05	0.03	0.05	5	0.02-0.44	0.05	0.44
1,2,3,4,7,8-HxCDF	4	0.01-0.03	0.01	0.03	3	0.01-0.23	0.05	0.23
1,2,3,6,7,8-HxCDF	3	0.01-0.015	0.01	0.01	2	0.02-0.06	0.04	0.06
1,2,3,7,8,9-HxCDF	0	--	--	--	1	--	0.02	--
2,3,4,6,7,8-HxCDF	0	--	--	--	3	0.01-0.03	0.02	0.03
1,2,3,4,6,7,8-HpCDF	2	0.02-0.023	0.02	0.02	1	--	0.05	--
1,2,3,4,7,8,9-HpCDF	0	--	--	--	1	--	0.02	--
OCDF	0	--	--	--	2	0.02-0.03	0.02	0.03

Also noteworthy, highest maximum concentrations of all detected PCDD/F congeners were observed in samples from Asia. Interestingly, these results contrast with previous analyses of PCBs from the same samples in which the highest concentrations were observed in farm-raised shrimp from the U.S., Belize, and Panama (i.e. all North American countries).<sup>7</sup> OCDD had the highest measured levels among all detected congeners regardless of region. Furthermore, maximum concentrations of detected TCDF and penta- and hexa-CDFs were 4-18 times higher in Asian samples compared to North American samples (data not shown).

We also assessed whether any clear patterns of detected congeners might exist in the samples with the highest measured PCDD/F concentrations. Figure 2 summarizes the characteristics of ten such samples, all of which had detected concentrations greater than 2 pg/g. Of these, 50% were wild-caught and 50% were farm-raised. Similarly, 50% were from Asian countries, and 50% were from North American countries. Three of the four samples with the highest PCDD/F concentrations were from Indonesia, and interestingly, they were obtained from three separate, independent grocers in the San Francisco area. As expected, OCDD concentrations were highest for most samples, followed by HpCDD concentrations. The patterns of congener concentrations in these samples were reasonably consistent, with the exception of one farm-raised sample from Indonesia which had a very different profile. In this sample, TCDF concentration was highest, followed by 1,2,3,7,8-PeCDF.

**Figure 2: Ten samples with the highest PCDD/F concentrations (pg/g wet weight)**



As noted above, several PCDD/F congeners were present in wild-caught North American shrimp that were not present in North American farmed shrimp. This suggests that different PCDD/F sources are contributing to wild shrimp loadings compared to farm-raised shrimp in North American countries. However, the congener patterns in the wild North American shrimp are not suggestive of any particular type of source. Similarly, the presence of several PCDD/F congeners in Asian farmed shrimp that are absent from Asian wild-caught shrimp suggests that one or more PCDD/F sources have contributed to the loadings, but the data, as presented here, do not permit any firm conclusions as to the potential nature of these sources.

### Acknowledgements

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