Measurements of PCDD and PCDF Concentrations in Wild-Caught and Farm-Raised Shrimp from the U.S. Retail Market

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BACKGROUND AND OBJECTIVES

Numerous studies have demonstrated that exposure to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) occurs through a number of different pathways.[1,2] 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.[3] Since an estimated four million tons of shrimp are consumed annually worldwide,[4] 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.[5,6] Additionally, several shrimp samples from North American countries had higher PCB concentrations than expected.[7] 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

- Eighty-four shrimp samples (uncooked, warm-water) purchased from local fish markets, supermarkets, and grocery stores in the San Francisco and Sacramento areas between February and April 2009.
  - Twenty-seven percent (n=23) were wild-caught.
  - Sixty-nine percent (n=58) were farm-raised.
  - Four percent (n=3) were not identified as wild-caught or farm-raised.
- The shrimp originated from 14 countries in three continents.
  - Fifty-seven percent (n=48) were from Asia.
  - Thirty-two percent (n=27) were from North America.
  - Ten percent (n=8) were from South America.
  - One percent (n=1) was from an unknown country of origin.
- 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) 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 95th 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 management and analyses were conducted using Microsoft Excel and SAS software (Cary, NC).

RESULTS

- Both farm-raised and wild-caught shrimp had an average of two detected congeners each, and the average number of detected congeners did not vary between these two groups (p=0.461).
  - Detection limits 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/F congeners.
  - Sixty percent (n=50) of all shrimp samples had between one and three detected congeners.
  - Seventeen percent (n=14) of all shrimp samples had between four and seven detected congeners.
  - Four percent (n=4) of all shrimp samples had eight or more detected PCDD/F congeners.

RESULTS CONTINUED

- Numerous PCDD/F congeners were detected in Asian and North American samples that were absent from the South American samples (Figure 1).
  - OCDD was the predominant congener detected in shrimp from all three continents, which is similar to PCDD/F congener profiles previously reported in cephalopods and shellfish from Spain.[8]- TCDD was detected in only one wild-caught sample from Asia.
  - 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).
  - 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.

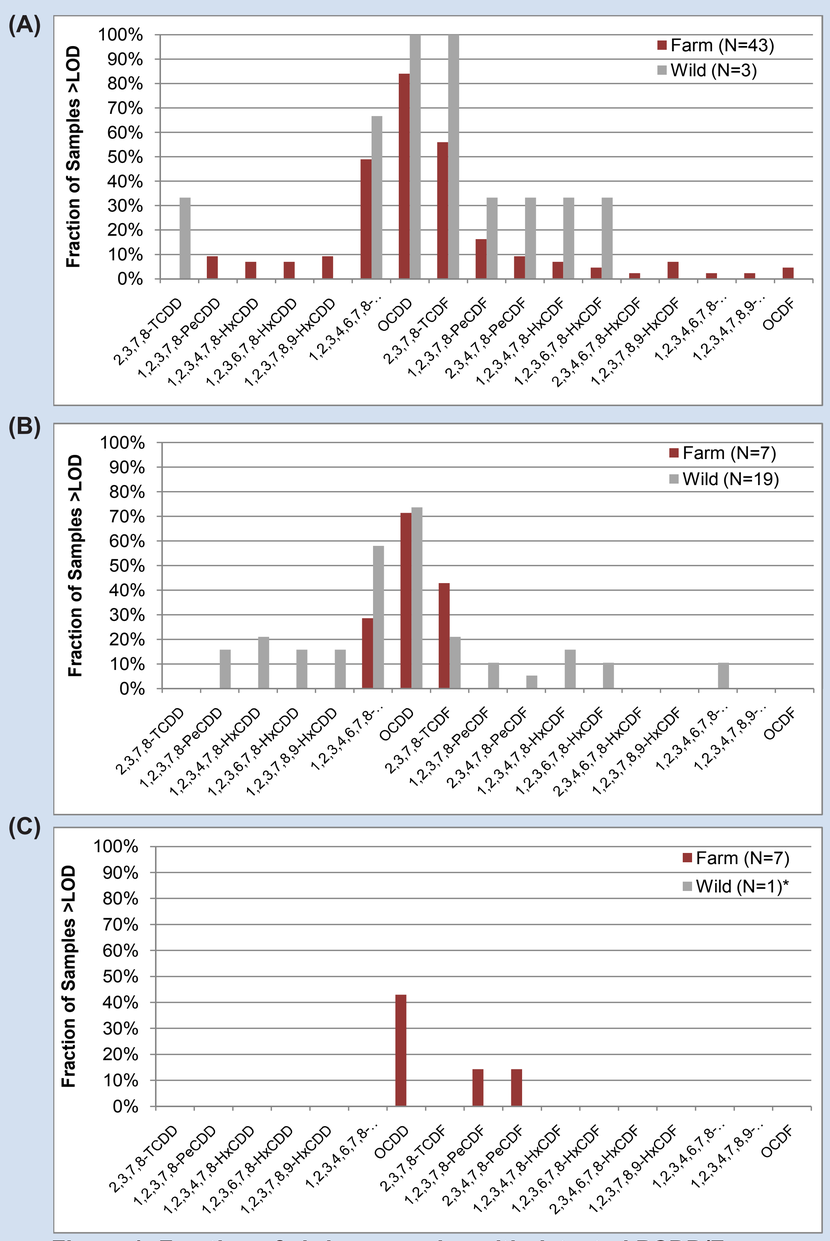

Figure 1: Fraction of shrimp samples with detected PCDD/F concentrations for (A) Asia, (B) North America, and (C) South America

- 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 (Table 1).
  - 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.
  - 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).
  - Median HpCDD concentration differed by sample type and was four times higher in wild-caught compared to farm-raised shrimp.
  - Maximum HpCDD concentration 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.

RESULTS CONTINUED

- Detected congener patterns were reasonably consistent among the ten samples with the highest concentrations, all of which were greater than 2 pg/g (Figure 2).
  - Fifty percent were wild-caught and 50% were farm-raised.
  - Fifty percent were from Asian countries, and 50% were from North American countries.
  - OCDD concentrations were highest for most samples, followed by HpCDD concentrations.
  - One farm-raised sample from Indonesia which had a very different profile than the others. In this sample, TCDF concentration was highest, followed by 1,2,3,7,8-PeCDF.
  - Three of the four samples with the highest PCDD/F concentrations were from Indonesia, and were obtained from three separate, independent grocers in the San Francisco area.

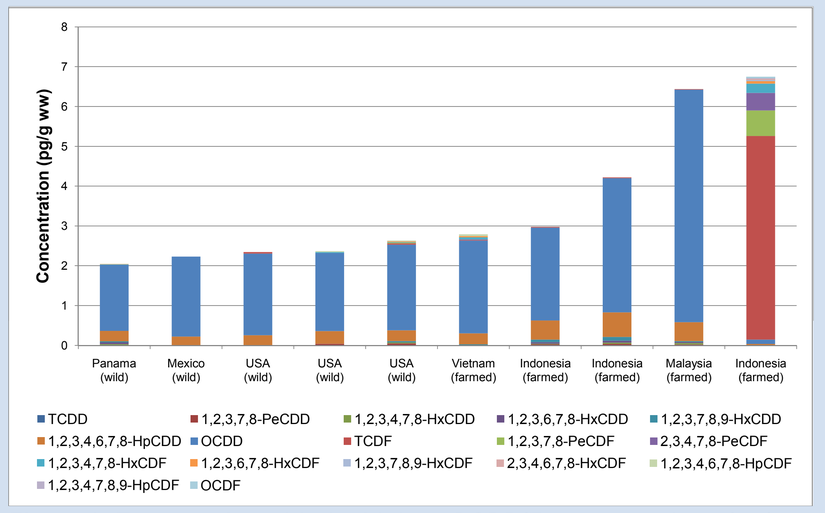

Figure 2: Ten samples with the highest PCDD/F concentrations (pg/g wet weight)

CONCLUSIONS

- 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.
- The highest maximum concentrations of all detected PCDD/F congeners were observed in samples from Asia, which contrasts 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).[7]
- 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.
- The PCDD/F 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.

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	0.2	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	0.3
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

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REFERENCES

Available upon request.