PCDD/Fs, PCBs, AND PBDEs IN CATFISH FROM U.S. COMMERCE

Huwe, JK[1], Esteban, E[2], Miller, O.[3]

[1] USDA, ARS, Biosciences Research Laboratory, 1605 Albrecht Blvd, Fargo, ND, 58102 USA
[2] USDA, FSIS, Office of Public Health Science, 950 College Station Rd, Athens, GA, 30605 USA
[3] USDA, FSIS, OFO, Catfish Inspection Staff, 1400 Independence Ave, SW Washington, DC, 20250 USA

Introduction

The U.S. Department of Agriculture (USDA) is responsible for the safety of meat, poultry, and egg products marketed in the United States. As such the USDA has conducted statistical surveys for dioxin-like compounds (PCDDs, PCDFs, and PCBs) in domestic meat and poultry over the past decade. [1,2] Recently the USDA Food Safety and Inspection Service (FSIS) proposed regulations for mandatory inspection of catfish and catfish products. Because little background data are available on environmental contaminant levels in catfish sold in the United States, an exploratory assessment of catfish products for the presence of PCDDs, PCDFs, PCBs, and polybrominated diphenyl ethers (PBDEs) was undertaken. Data from this survey will be used to determine background levels of these contaminants in domestically marketed catfish. In addition, the data may be used by risk assessors to estimate human exposure to PCDDs, PCDFs, PCBs, and PBDEs from consumption of retail catfish in the United States.

Materials and Methods

Catfish (N = 202) were collected under the Pesticide Data Program[3] in 2009. The catfish included nuggets and fillets collected at markets and large distribution centers located across the U.S. in a statistically-designed manner to reflect what is typically available for consumption. Catfish samples were skinned (if necessary), homogenized, and analyzed for PCDDs, PCDFs, 12 dioxin-like PCBs (dl-PCBs), 6 indicator PCBs (nos. 28, 52, 101, 153, 138, and 180), and sixteen PBDEs (nos. 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 201, 203, 206, 207, and 209) by isotope dilution high resolution GC/MS methods based on EPA Methods 1613, 1668A, and 1614. Briefly, catfish (10 g) were spiked with ^{13}C-labeled standards, extracted with dichloromethane in a tissumizer, fractionated by column chromatography on a Power Prep system (Fluid Management Systems, Waltham, MA, USA), and analyzed by HRGC-HRMS using either a 60 m DB-5ms column (PCDD/PCDF/*non-ortho*-PCBs), a 30 m DB-1ms column (PCBs), or a 15 m DB-5ms column (PBDEs). The analytical methods were validated by successful participation in an interlaboratory comparison of PCDDs, PCDFs, PCBs, and PBDEs in foods and by replicate analyses of spiked method blanks and one representative catfish sample. Several congeners (PCB-123 and nona- and deca-BDEs) were not detected above our detection limit (3 standard deviations above background mean) in >96% of the catfish samples and so are not included in the totals. TEQs were calculated using the 2005 WHO TEFs.

Results and Discussion

The USDA Pesticide Data Program (PDP) is an annual program in which various food commodities in the U.S. are tested for pesticide residues. In the 2009 PDP, catfish were collected for pesticide residue testing, and a subset (202 of the 744 samples) was randomly chosen for PCDD, PCDF, PCB, and PBDE analysis.

Table 1 summarizes the mean, median, and range of concentrations for PCDD/F TEQ, dl-PCB TEQ, the sum of 6 indicator PCBs, and the sum of PBDE congeners measured in the catfish. The 5 major PBDEs (no. 47, 99, 100, 153, and 154) accounted for 81% of the average total PBDEs detected and are used for comparison to other studies. PCDD/F TEQ ranged from not detected to 3.46 ppt wet weight. The dl-PCB TEQ was lower and averaged about 10% of the PCDD/F value. The persistent indictor PCB concentration ranged from 9.6 – 1383 pg/g wet weight and averaged three-fold higher than the PBDE sum.

In general, all values were lower than a previous study which reported concentrations of these persistent organic pollutants in both wild-caught and farm-raised catfish from Mississippi (MS) in 2006.[4,5] Concentrations measured in the 2006 MS study had medians of PCDD/F/dl-PCB TEQ = 1.0 pg/g, sum of 97 PCBs = 1300 pg/g, and sum of 5 PBDEs = 280 pg/g (estimated from the data provided) in the farm-raised catfish (N = 28). This study also found that wild-caught catfish had significantly higher levels of PCBs and PBDEs on a wet weight

basis than the farm-raised fish. The concentrations in the 2009 PDP catfish may be lower than the 2006 MS farm-raised catfish due to either a geographical difference or to the smaller size of the 2006 study compared to the PDP study.

The PCDD/F congener pattern was similar in both the 2006 MS farm-raised catfish and the 2009 PCP catfish. Figure 1 shows the average pattern for both studies and also the congener pattern found in catfish associated with a ball clay contamination episode in the mid-1990s.[6] Although TEQ levels were much higher in the ball clay exposed catfish (6 – 43 pg TEQ/g), the congener patterns are remarkably similar suggesting an on-going, although much lower, exposure to ball clay or a similar material. This low exposure may be due to small amounts of ball clay still added to fish feeds or due to residual ball clay present in the sediments of catfish ponds. Nonetheless, the TEQ levels found in catfish in U.S. commerce are generally low.

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Table 1. Mean, median, and range of TEQs[1], sum of 6 indicator PCBs, sum of 5 major PBDEs, and sum of 13 tri- to octa-BDEs (pg/g wet weight) for catfish collected from the U.S. market in 2009. Values assume nondetects = LOD/2 (data calculated with nondetects = 0 are in parentheses).

	PCDD/F TEQ	dl-PCB TEQ	Sum 6-PCBs[2]	Sum 5-PBDEs[3]	Sum 13-PBDEs[4]
Mean	0.28 (0.27)	0.02 (0.02)	182 (182)	57 (55)	68 (63)
Median	0.08 (0.08)	0.01 (0.01)	134 (134)	45 (45)	53 (50)
Range	0.02 – 3.46	0.001 – 0.10	9.6 – 1384	8.1 – 266	12.4 – 290

[1] TEQs were calculated using WHO2005 TEFs.
[2] Sum of PCBs-28, 52, 101, 138, 153, and 180.
[3] Sum of BDEs-47, 99, 100, 153, and 154.
[4] Sum of BDEs-28, 66, 47, 85, 99, 100, 153, 154, 183, 196, 197, 201, and 203.

Figure 1. Average relative contribution of individual congeners to the sum of PCDD/Fs in the 2009 PDP survey catfish, in farm-raised catfish from MS in 2006[4], and in farm-raised catfish from a ball clay contamination episode in 1995 in Southeastern U.S.[6]