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Dioxin congener patterns in commercial catfish from the United States and the indication of mineral clays as the potential source

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Since 1991 the US Department of Agriculture (USDA) has conducted annual surveys of pesticide residues in foods under the Agricultural Marketing Service's Pesticide Data Program (PDP). To assess chemical residues in domestically marketed catfish products, 1479 catfish samples were collected during the 2008–2010 PDPs. A subset of 202 samples was analysed for 17 toxic polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). The average pattern of the individual PCDD/F congener concentrations in the catfish was rather unique in that it had almost no measurable amounts of polychlorinated dibenzofurans (PCDFs), but all PCDDs were present. This pattern was more dominant in the domestically produced catfish products than in the imported products (China/Taiwan). Comparison of the pattern to known sources of PCDD/Fs showed strong similarities to the pattern of PCDD/Fs found in kaolin clays which have often been used as anti-caking agents in animal feeds. To investigate whether catfish feeds may be the source of the PCDD/Fs found in the catfish, archived catfish feed data from a US Food and Drug Administration (USFDA) database were examined. In 61 out of 112 feed samples, the PCDD concentrations were 50 times higher than the PCDF concentrations and resembled the pattern found in the catfish products and in clays mined in the south-eastern United States. Although the source of PCDD/Fs in domestically marketed catfish products cannot be definitively established, mined clay products used in feeds should be considered a likely source and, given the wide concentration range of PCDD/Fs that has been found in clays, a critical control point for PCDD/Fs entrance to the food supply.

Keywords: dioxins; catfish; feeds; kaolin clay; congener pattern

Introduction

Since 1991, the US Department of Agriculture (USDA) has conducted annual surveys of pesticide residues in foods under the Agricultural Marketing Service's (AMS) Pesticide Data Program (PDP) (AMS PDP 1992–2012). Because the PDP is a statistically based sampling programme, the food products and the incurred levels of residues reflect typical consumption amounts for the general US population and can be used for estimating chemical exposures. Few data are available on the levels of hazardous chemicals, such as environmental contaminants, heavy metals and veterinary drugs, in catfish products sold in the United States, and inclusion in the PDP was a logical approach to conduct an assessment of these chemical residues in domestically marketed catfish products. Therefore, catfish products were collected from retail markets during the 2008–2010 PDPs and analysed for pesticides, heavy metals, veterinary drugs and certain environmental contaminants.

The environmental contaminants included in the assessment were polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs). Each of these classes of chemicals is characterised as toxic, persistent, bioaccumulative and globally transported and is listed as persistent organic pollutants scheduled for elimination under the Stockholm Convention (2008–2012). PCDD/Fs are considered especially hazardous. Unlike PCBs and PBDEs which were manufactured chemicals, PCDD/Fs are unintentional by-products of incineration processes and pesticide manufacturing. Of the 210 possible PCDD/F congeners, only the seventeen 2,3,7,8-chloro-substituted congeners are considered toxic and bioaccumulative. These 17 congeners have a range of toxic potency, and each has been assigned a toxic equivalency factor (TEF) based on the relative potency compared with the most toxic congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (van den Berg et al. 2006). A toxic equivalent (TEQ) is then defined as the summation of all toxic congener concentrations weighted by their TEF to provide a single unit to measure the toxic concentration of all the PCDD/Fs.

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Based on this toxicity measurement system, European and Asian countries have set regulatory levels for PCDD/F TEQs in foods. In fish the European Union action level for PCDD/F TEQ is $3.0\,pg\,g^{-1}$ muscle (Commission of the European Communities (CEC) 2006). The US Environmental Protection Agency (USEPA) recently established a daily reference dose for TCDD, the most toxic PCDD, at $0.7\,pg\,kg^{-1}$ body weight (USEPA 2012). While no food tolerance levels have been set in the United States, lowering levels in foods and animal feeds is strongly recommended (Institute of Medicine (IOM) of the National Academies 2003).

The USDA has conducted statistically based surveys of PCDD/Fs in domestic meat and poultry over the past two decades to determine levels, investigate trends and uncover sources (Hoffman et al. 2006; Huwe et al. 2009); however, catfish products were not included. Smaller market basket surveys (Fiedler et al. 1998; Jensen & Bolger 2001) conducted in the mid-1990s showed that some catfish marketed in the United States contained elevated levels of PCDD/Fs ($>5\,pg\,g^{-1}$ muscle) which were later ascribed to a contaminated feed ingredient, ball clay (Rappe et al. 1998; Hayward et al. 1999). To investigate the current levels of PCDD/Fs and other POPs in catfish in the United States, a statistically based survey was conducted. The quantitative PCDD/F, PBDE and PCB data collected in these 2008–2010 PDP surveys represent the best assessment of the current levels of these contaminants in catfish marketed in the United States, and a summary of these data has been reported previously (Huwe et al. 2011). In this paper we discuss the concentrations of individual PCDD/F congeners and the possible sources of PCDD/Fs in commercial catfish as indicated by the congener patterns.

Materials and methods

Between April 2008 and June 2010 under the USDA AMS PDP, 1479 samples identified as "catfish" (fillets, nuggets, strips and steaks) were collected from retail markets and large distribution centres located across the United States for residue testing. Catfish were categorised as domestic or imported based on the product label. Further details of the collection scheme can be found in the PDP Annual Summaries, Calendar Years 2008–2010 (AMS PDP 2008–2012). A subset of the catfish products ($N = 202$) collected between July 2009 and May 2010 was randomly chosen and analysed for all (tetra- to octa-) PCDDs and PCDFs in addition to 12 dioxin-like PCBs (dl-PCBs), six indicator PCBs (numbers 28, 52, 101, 153, 138 and 180), and 16 PBDEs (numbers 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 201, 203, 206, 207 and 209). A summary of the PCDD/F, PBDE and PCB analyses and results was published previously (Huwe et al. 2011); the PCDD/F data will be discussed in more detail below.

Catfish samples were skinned, if needed, homogenised, and aliquots (10 g) were purified and analysed by a method based on USEPA Method 1613 (USEPA 1994) as previously described (Hoffman et al. 2006; Huwe et al. 2009). Briefly, samples were extracted with dichloromethane in a tissumiser, fractionated by column chromatography on a Power Prep™ system (Fluid Management Systems, Watertown, MA, USA), and analysed by high-resolution gas chromatography-high resolution mass spectrometry using a 60 m DB-5 ms column. The analytical method was validated by successful participation in an inter-laboratory comparison in foods and by replicate analyses of spiked method blanks and one representative catfish sample. Method detection limits (DL) varied for each congener and ranged from $0.01–0.23\,pg\,g^{-1}$ for individual PCDD/Fs (Table 1). TEQ values were calculated using the 2005 World Health Organisation (WHO) TEFs (van den Berg et al. 2006). All results are reported on a whole-weight basis with non-detects equal to half the DL, except for congener pattern graphs where non-detects were set to zero so that DLs would not contribute to the pattern.

Of the 202 catfish products analysed for PCDD/Fs, 148 samples were domestically produced, 52 were imported and two were of unknown origin. Catfish feed data were obtained from the US Food and Drug Administration (USFDA) database. The feed had been analysed for 2,3,7,8-substituted PCDD/Fs following a method based on USEPA Method 1613 (USEPA 1994).

Results

Table 1 shows the concentrations and detection rates of the individual 2,3,7,8-substituted PCDD/Fs in the catfish. Being ubiquitous environmental contaminants, PCDDs and/or PCDFs were detected in 96% of the catfish products. PCDDs were detected more often than PCDFs and, generally, in higher concentrations. The ratio of 2,3,7,8-substituted PCDDs to PCDFs (D:F) averaged 54 when non-detects were set to half the detection limits but >450 when non-detects were set to zero (data not shown) due to the low detection rates of many PCDFs. TCDF and penta- (Pe), hexa- (Hx), hepta- (Hp), and octa- (O)CDDs were the most often detected congeners ($>64\%$ detection rates), while OCDF was never detected. HpCDD and OCDD had the highest mean concentrations and, on average, accounted for $11\% \pm 2.7\%$ and $59\% \pm 21.0\%$ of the total PCDD/F concentration, respectively. From a toxicity basis, PeCDD accounted for the largest portion of the TEQ (44%) followed by TCDF,

Table 1. Concentrations (pg g^{-1} wet weight), detection rates, and detection limits of individual 2,3,7,8-substituted PCDDs and PCDFs and the ratio of the 2,3,7,8-substituted PCDDs to PCDFs (*D*:*F*) in commercial catfish. Non-detects were set to half the detection limit for calculation of means and medians.

Congener	Range (pg g^{-1} w/w)	Mean ± SD (pg g^{-1} w/w)	Median (pg g^{-1} w/w)	Percentage of detects	Detection limit (pg g^{-1} w/w)
2,3,7,8-TCDF	0–0.12	0.02 ± 0.01	0.01	69.3	0.008
1,2,3,7,8-PeCDF	0–0.10	0.01 ± 0.01	0.01	21.3	0.018
2,3,4,7,8-PeCDF	0–0.18	0.02 ± 0.02	0.01	22.3	0.021
1,2,3,4,7,8-HxCDF	0–0.09	0.02 ± 0.01	0.02	10.4	0.032
1,2,3,6,7,8-HxCDF	0–0.07	0.01 ± 0.01	0.01	22.8	0.015
2,3,4,6,7,8-HxCDF	0–0.06	0.01 ± 0.01	0.01	22.3	0.013
1,2,3,7,8,9-HxCDF	0–0.03	0.01 ± 0.004	0.004	5.9	0.008
1,2,3,4,6,7,8-HpCDF	0–0.10	0.03 ± 0.01	0.03	6.9	0.053
1,2,3,4,7,8,9-HpCDF	0–0.04	0.01 ± 0.01	0.01	9.4	0.013
OCDF	0–0	0.07 ± 0.0	0.07	0.0	0.131
2,3,7,8-TCDD	0–0.34	0.04 ± 0.05	0.01	48.5	0.013
1,2,3,7,8-PeCDD	0–2.03	0.15 ± 0.28	0.05	70.8	0.013
1,2,3,4,7,8-HxCDD	0–2.25	0.16 ± 0.31	0.03	64.4	0.011
1,2,3,6,7,8-HxCDD	0–3.50	0.25 ± 0.48	0.06	72.8	0.011
1,2,3,7,8,9-HxCDD	0–3.27	0.21 ± 0.45	0.04	64.9	0.012
1,2,3,4,6,7,8-HpCDD	0–19.57	1.36 ± 2.69	0.21	76.2	0.049
OCDD	0–85.6	7.87 ± 14.5	1.23	73.3	0.227
PCDFs	0–0.71	0.2 ± 0.07	0.17	77.7	
PCDDs	0–116.5	10.0 ± 18.5	1.67	86.1	
PCDD/Fs	0–116.7	10.2 ± 18.5	1.93	96.0	
Ratio *D*:*F*	0–662.3	53.9 ± 99.2	9.24		

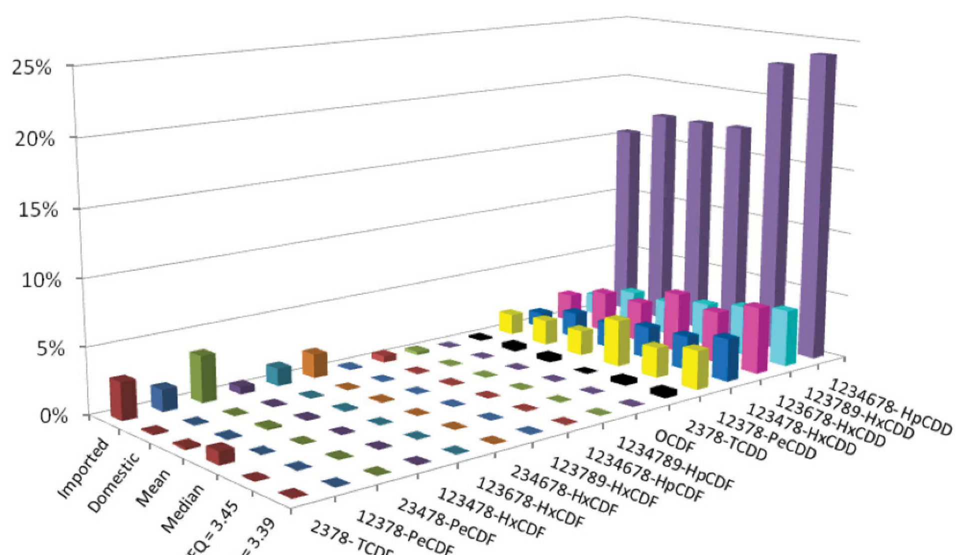

Figure 1. Per cent contributions of individual 2,3,7,8-substituted congeners normalised to OCDD (OCDD = 100%) for two catfish samples with TEQs > 3 pg g^{-1} wet weight, for the mean and median values of all PDP catfish ($N = 202$), and for the mean values of the domestic ($N = 146$) and imported ($N = 52$) products.

1,2,3,7,8-PeCDF, TCDD, and 1,2,3,6,7,8-HxCDD (8–9% each), on average.

Congener and homologue patterns were initially assessed in the two catfish samples with the highest TEQs (=3.45 and 3.39 pg g^{-1} w/w); the patterns are shown in Figures 1 and 2. These two samples also had the highest *D*:*F* ratios, 662 and 526, and OCDD comprised > 70% of the total PCDD/F concentration in each. Similar congener patterns, which were dominated by PCDDs, were also observed for the mean and median values in the catfish (Figure 1). Non-2,3,7,8-substituted PCDD/Fs were observed in many of the samples near the limits of detection (estimated non-2,3,7,8-homologue medians were 0.01–0.1 pg g^{-1} w/w).

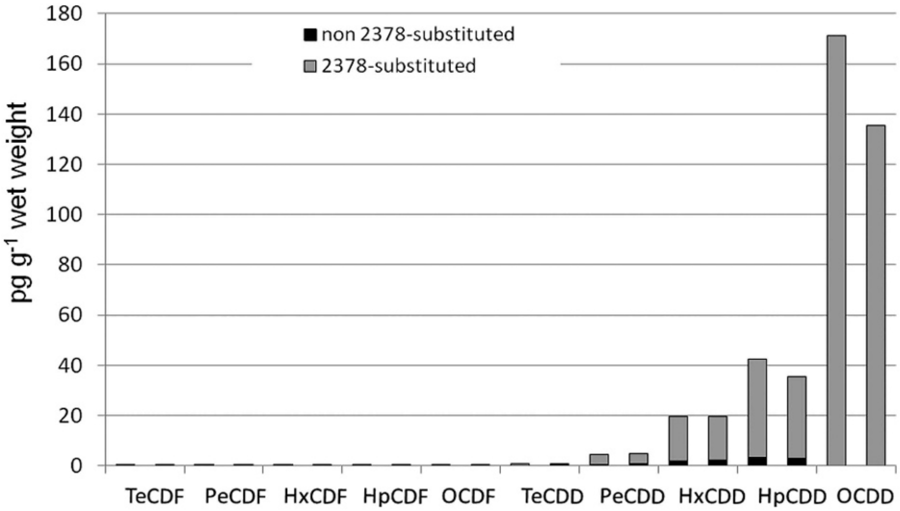

Figure 2. Homologue profiles of two catfish with TEQs $>3\,\mathrm{pg\,g^{-1}}$ wet weight.

The catfish samples with the highest concentrations of PCDDs had measurable non-2,3,7,8-congeners analogous to those observed by Fiedler et al. (1998). For example, in the two samples with the highest PCDD (and TEQ) concentrations, non-2,3,7,8-substituted dioxins comprised $<30\%$ of the tetra, $<16\%$ of the penta, $<12\%$ of the hexa, and $<9\%$ of the hepta homologue concentrations (Figure 2).

A comparison of congener patterns based on the country of origin (domestic versus imported) showed somewhat more furans in imported products than in domestic products (Figure 1), but OCDD still had the highest average concentration. Most of the imported catfish products (48 out of 52) were from China or Taiwan. Average TEQs in imported products were significantly lower than in domestic products, $0.03 \pm 0.07\,\mathrm{pg\,g^{-1}}$ w/w compared with $0.35 \pm 0.54\,\mathrm{pg\,g^{-1}}$ w/w ($p < 0.001$, Student's t-test), and average D:F ratios were 5.2 ± 27.5 in imported and 71.1 ± 109.6 in domestic products. The largest contributor to TEQ in imports was 2,3,4,7,8-PeCDF (29%), and in domestic products it was 1,2,3,7,8-PeCDD (54%). Together these differences suggest different or additional sources of PCDD/F contamination in the US and Chinese/Taiwan catfish.

Discussion

Although the USDA PDP reflects typical consumption patterns for the general US population, it incorporates no ability to trace products from the country of origin to the specific site of production. No feeds or environmental samples associated with the catfish products were obtained from production sites. Therefore, speculation on the source(s) of dioxin contamination for the catfish in this study was limited to observations and interpretations of the congener profiles and patterns.

PCDD/F congener patterns and profiles are often unique to their source, and major sources have been characterised and catalogued (Rappe 1994; Cleverly et al. 1997). Congener patterns have also been used to track and attribute sources in food contamination incidents in spite of the fact that absorption and metabolism of individual PCDD/Fs in animal systems can significantly change the congener pattern. For example, classic patterns of PCDD/Fs produced by incineration have been reported in milk from cows raised near a municipal waste incinerator (Slob et al. 1995) and from buffalo raised in areas where high rates of illegal waste burning have occurred (Esposito et al. 2010). This congener pattern is dominated by penta- and hexa-congeners, has a D:F ratio of approximately 0.5, and 2,3,4,7,8-PeCDF contributes most to the TEQ. In the Belgium dioxin incident of 1999, a low D:F ratio (0.06) pointed to a PCB contamination which was confirmed by an extremely high PCB to PCDD/F ratio ($>50{,}000$) (van Larebeke et al. 2001). The predominance of hepta- and octa-CDD/Fs and 1,2,3,6,7,8-HxCDD suggested pentachlorophenol as the source of contamination in a choline chloride incident in Europe (Llerena et al. 2003) and in US cattle with access to pentachlorophenol-treated wood (Huwe et al. 2004). Finally, contaminated ball clay used in animal feeds resulted in an unusual congener pattern in chicken and catfish products which was dominated by OCDD, had a D:F ratio >50, and had major contributions from 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD to the TEQ (Fiedler et al. 1998; Hayward et al. 1999; Ferrario & Byrne 2000).

Of the congener patterns associated with known sources, the PDP catfish products most resembled the ball clay source with one major exception, i.e. minimal

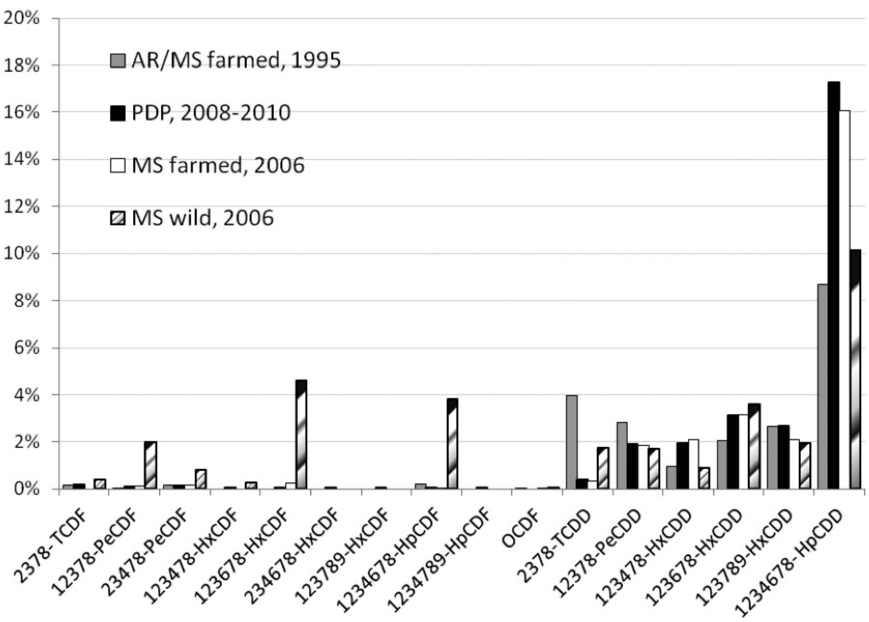

Figure 3. Per cent contributions of individual congeners normalised to OCDD (OCDD = 100%) for the mean values of catfish collected from Arkansas and Mississippi (AR/MS) farms during the ball clay incident in 1995 (Fiedler et al. 1998), under the Pesticide Data Program (PDP) in 2008–2010 (present study), and from Mississippi farms and Mississippi rivers (wild) in 2006 (Scott et al. 2009).

levels of TCDD (Figure 3; data graphed from Fiedler et al. 1998). This same congener pattern was observed in farm-raised catfish from Mississippi in the United States, but not in wild fish from Mississippi (Figure 3; data graphed from Scott et al. 2009). Because the majority of PDP samples were domestic and because Mississippi and three neighbouring states account for >90% of US catfish production (National Agricultural Statistics Service (NASS) 1988–2012), it is not surprising that the patterns are similar between the PDP and Mississippi farm-raised samples and may reflect a similar source of PCDD/Fs. The wild Mississippi fish displayed a congener pattern containing more furans and suggested another source(s) of PCDD/Fs more like the classic incinerator pattern.

When the PDP catfish were sorted by D:F ratios (D:$F < 1$ and > 50), two distinct patterns were observed (Figure 4). Samples that had a D:F ratio > 50 ($N = 57$) showed the same congener pattern that dominated in the PDP catfish indicative of ball clay. This group was comprised of 96% domestic products and had an average TEQ of $0.80 \pm 0.67\,\text{pg}\,\text{g}^{-1}$ w/w. Those samples that had a D:F ratio < 1 ($N = 27$) had a significantly lower TEQ than the high ratio group ($0.05 \pm 0.03\,\text{pg}\,\text{g}^{-1}$ w/w; $p < 0.001$, Student's t-test) and might be considered representative of the "background" PCDD/F contamination in commercial catfish. This group was comprised of 93% imported products.

Ball clay is a specific type of kaolin which, due to its physical properties, has been used as an anti-caking agent in animal feeds. While kaolins have widely distributed TEQ content, the homologue profiles and congener patterns are uniquely similar (Horii et al. 2011; Schmitz et al. 2011). Two characteristics of the congener pattern are the lack of PCDFs and the predominance of 1,2,3,7,8,9-HxCDD over 1,2,3,6,7,8-HxCDD. In the PDP catfish the ratio of 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD averaged 0.96 ± 1.03. Uptake and metabolism differences of these two congeners in the catfish may explain the lack of dominance of 1,2,3,7,8,9-HxCDD. Facile metabolism of the non-persistent (non-2,3,7,8-substituted) congeners also accounts for the low levels of these compounds found in the catfish. When fish and their corresponding feeds were analysed during the ball clay incident in the mid-1990s, the ratio of 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD was found to decrease by 40% from feed to fillets and levels of non-2,3,7,8-congeners were greatly reduced from feed to fillets (Fiedler et al. 1998). Therefore, the congener pattern in the domestic catfish from the 2008–2010 PDP is consistent with the kaolinic clay pattern, and two possible sources are the catfish feeds or the rearing pond sediments.

During the ball clay incident in the south-eastern United States, it was noted that lake and river sediments from Mississippi had similar congener profiles to the contaminated feeds suggesting that local clay may be the common source (Rappe et al. 1998). Whether clay in feed or clay in the sediments is the major PCDD/F exposure source to commercial catfish today cannot be definitively determined from the data because the PDP provided no ability to track back and

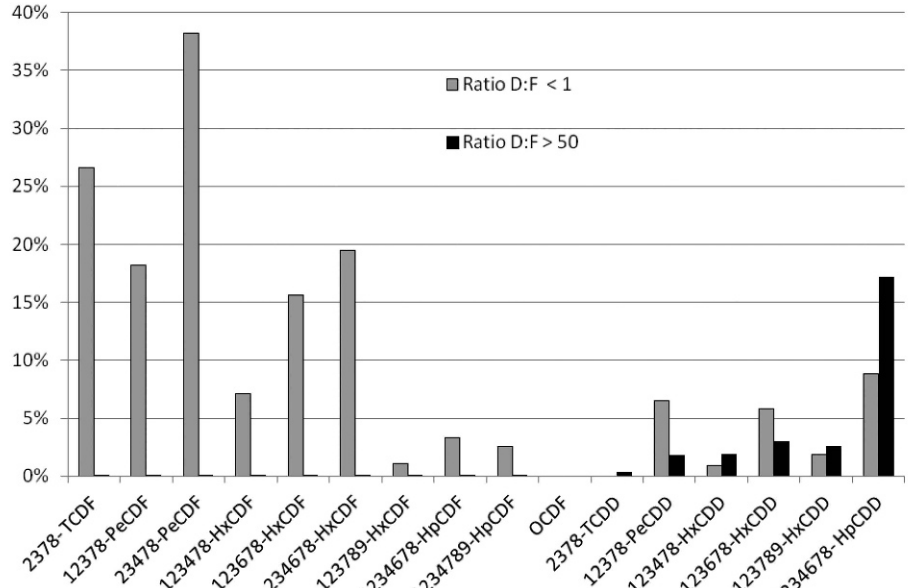

Figure 4. Per cent contributions of individual 2,3,7,8-substituted congeners normalised to OCDD (OCDD = 100%) for the mean values of products with *D*:*F* ratios <1 (*N* = 27) and >50 (*N* = 57).

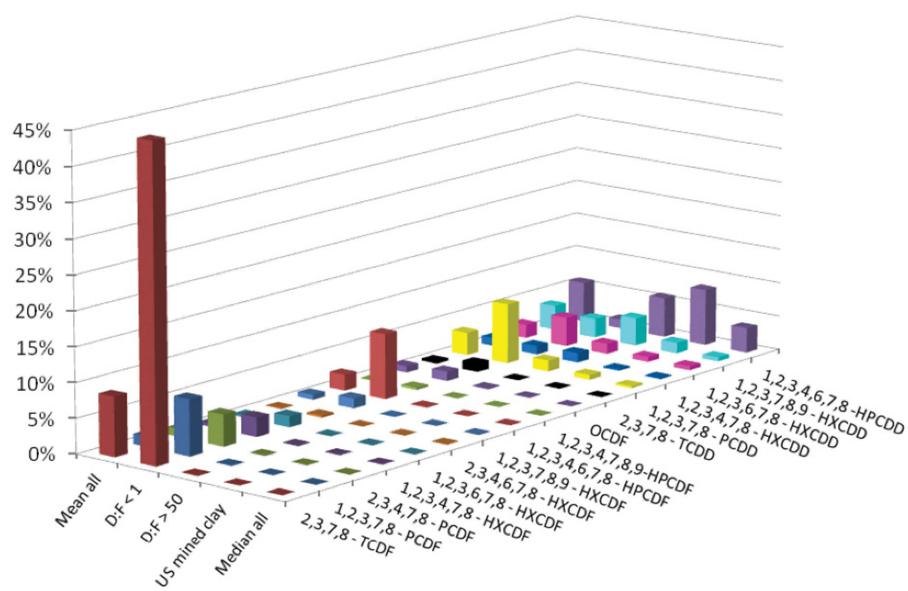

Figure 5. Per cent contributions of individual congeners to total concentration (OCDD not shown) for the mean of all catfish feeds from the USFDA database (*N* = 112), the catfish feeds with *D*:*F* ratios <1 (*N* = 17), the catfish feeds with *D*:*F* > 50 (*N* = 61), and the mined clays from the south-eastern United States used in animal feeds (*N* = 9) (Ferrario et al. 2000), and the median for all USFDA catfish feeds.

investigate the actual production sites of catfish samples. To investigate catfish feed as a potential source of the dioxins, we obtained archived catfish feed data from a USFDA database and examined the congener patterns.

The USFDA database contained quantitative levels of the seventeen 2,3,7,8-substituted PCDD/Fs from 112 domestic catfish feeds collected over the years 2001–2009. These samples were not associated with any contamination episodes, and, therefore, reflected typically marketed feeds. The feeds had PCDD/F TEQs ranging from not detected to 2.0 $pg\,g^{-1}$ w/w. OCDD was the dominant congener averaging 67.8% of the total PCDD/F concentration, followed by HpCDD (5.8%). The ratio of *D*:*F*s ranged from zero to 14,000, and different congener patterns were observed in the mean and median values (Figure 5). When the feeds were sorted based on D:F ratios, 61 feed samples had ratios >50 which may be indicative of kaolin clays, and 17 samples had ratios <1 more indicative of an incineration pattern (Figure 5). Comparison of these congener patterns with the pattern reported by Ferrario et al. (2000) for mined clay products used in animal feeds showed the median values of all the catfish feeds and the mean values of those with a high D:F ratio resembled the mined clays (Figure 5).

The similarities in this pattern included OCDD accounting for $>85\%$ of the total concentration and PCDFs generally not detected. Two differences between the congener patterns of the feeds with high D:F and the clays were slightly higher contributions from penta- and hexa-CDDs and a few PCDFs (notably 1,2,3,4,6,7,8-HpCDF and OCDF) and a ratio <1 for 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD (mean ratio = 0.75) in the feeds. These differences likely result from other sources of PCDD/Fs contributing to the total feed residue.

Based on the congener patterns found in the catfish and catfish feeds, it seems likely that mined clay products are still used in catfish feeds and, in a few cases, may contribute to undesirable TEQ levels (up to 3.46 pg TEQ g^{-1} w/w measured in this study). While TCDD levels in the 2008–2010 PDP catfish products averaged almost 10-fold lower than in the catfish from the mid-1990s ball clay episode (0.89 versus 7.8 pg TCDD g^{-1} lipid), the average of the total PCDD/F TEQ was only three-fold lower (7.54 versus 21.8 pg TEQ g^{-1} lipid) and the range of TEQs exceeded that of the ball clay catfish (0.52–79.3 versus 7.0–50.5 pg TEQ g^{-1} lipid) (Fiedler et al. 1998; data converted with 2005 TEFs). Therefore, caution should be exercised in the use of clays in animal feeds, and kaolin clays should be considered a critical control point for entrance of PCDD/Fs into the food supply. Small amounts of mineral clays added to fish feeds together with residual clays present in the sediments of catfish ponds and other sources of PCDD/Fs to the feeds may lead to higher than acceptable dioxin residues in the final catfish products.

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