DIOXIN IN BALL CLAY AND KAOLIN

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Introduction

In 1997, we reported PCDD and PCDF concentrations for 43 food items purchased from local stores in Mississippi, USA (1). The three farm-raised catfish samples had the highest 2,3,7,8-tetraCDD concentrations (2.5-8.8 pg/g lipid) and the highest I-TEQ (10.2-27.8 pg/g I-TEQ) of all food items (1). The farm-raised catfish also contained remarkably high concentrations of the higher chlorinated dioxins and most non-2,3,7,8-substituted PCDD congeners.

Later, we purchased additional farm-raised catfish from the same manufacturer and catfish directly from farms in Mississippi, Arkansas, and Alabama. We also collected sediment from the Mississippi catfish ponds and catfish feed from the Mississippi and Arkansas farms. In 1998, we confirmed the results of our earlier study and found even higher 2,3,7,8-tetraCDD concentrations (32 and 27 pg/g lipid) and I-TEQ values (37-43 pg/g I-TEQ) in the two catfish from the Arkansas farm (2). In addition, our results clearly showed that the feed, and not the pond sediment, was the source of PCDDs to the farm-raised catfish (2).

We also reported the results of our analyses of the catfish feed, including each of the eight components of the feed (3). One of the catfish feed ingredients--the soybean meal--had extraordinarily high concentrations of all 2,3,7,8-substituted PCDDs and an I-TEQ value of 576 pg/g fat. Moreover, the congener pattern and the high Σ PCDDs/Σ PCDFs ratio for the soybean meal were unique; no environmental samples, chemical products, or known anthropogenic sources of PCDDs and PCDFs had a similar pattern or ratio. As a result, we suggested natural formation could be the source of PCDDs in the soybean meal (3).

Our results were later confirmed by Ferrario *et al.* who further determined that a ball clay added to the soybean meal was the primary source of PCDDs in the catfish feed (4). The United States Food and Drug Administration (US FDA) confirmed the ball clay was the source of PCDDs to the catfish feed and also found that the same soybean meal was a component in chicken feed (5). Hayward *et al.* also found PCDD patterns in chicken eggs that resembled the PCDD patterns in farm-raised catfish feed (6).

At Dioxin 2000, we presented PCDD and PCDF concentrations for four U.S. ball clay samples, three U.S. kaolin samples, and one German kaolin sample (7). In this study, we report PCDD and PCDF concentrations for four additional German kaolin samples, which confirm our earlier results.

Methods and Materials

In April, 2000, we obtained four kaolin samples from Germany. Seventeen internal standards were added to each sample, each sample was then Soxhlet-extracted with 150 mL of toluene. The extracts were purified first in a multistep silica column, followed by a basic alumina column. The final clean-up was made on a Carbopack/Celite column. The final extracts were evaporated in 30 μL of tetradecane. HRGC/HRMS analyses was performed on each sample with a 60 m JW DB-5 column directly attached to a VG instrument (70/70S).

Results

Table 1 includes significant 2,3,7,8-substituted PCDD and PCDF concentrations, the sum of the homologues, and both the I-TEQ and WHO-TEQ for the four new German kaolin samples and the previously reported ball clay and kaolin samples (7).

In general, the German kaolin resembled the U.S. ball clay, and not the U.S. kaolin from our earlier study. Specifically, four of the five German kaolin samples contained high PCDD concentrations. *See* Table 1. The mean 2,3,7,8-tetraCDD concentration of the German kaolin samples was 35 pg/g, and the highest concentration was 130 pg/g. The mean 1,2,3,7,8-pentaCDD concentration was 64 pg/g, and the highest concentration was 220 pg/g. The mean WHO-TEF value was 128 pg/g, and the highest value was 390 pg/g.

Discussion

The high PCDD concentrations in the U.S. ball clay and German kaolin confirm our earlier findings in farm-raised catfish and catfish feed. These results also confirm that ball clay added to the soybean meal in the feed is the source of these compounds. Moreover, our earlier hypothesis of a natural formation of PCDDs in ball clay (3) has now been observed by others (4, 6, 8). Our results here further confirm the natural formation of PCDDs and also show that this natural formation is not limited to the southern United States.

The tetra-, penta-, and hexaCDD patterns are similar for the U.S. ball clay and the German kaolin. For example, the U.S. ball clay and the German kaolin all contain 1,3,7,8-, 2,3,7,8-, 1,2,7,8- and 1,2,8,9-tetraCDDs. Likewise, these samples all contain 1,2,4,8,9- or 1,2,4,7,9-, 1,2,4,6,9-, 1,2,4,6,7-, or 1,2,4,8,9-, 1,2,3,7,8- and 1,2,3,8,9-pentaCDDs. Finally, the U.S. ball clay and the German kaolin all contain 1,2,4,6,7,9- or 1,2,4,6,8,9-, 1,2,3,6,7,9- or 1,2,3,6,8,9- and 1,2,3,7,8,9- hexaCDDs. This unique and non-anthropogenic pattern is present in ball clay from the southern United States and kaolin from Germany.

Notwithstanding the similar appearance of ball clay and kaolin, the U.S. kaolin contained very low concentrations of all 2,3,7,8-substituted PCDDs. 2,3,7,8-TetraCDD was not detected in any sample, and 1,2,3,7,8-pentaCDD was detected in only one sample (at 0.21 pg/g). The higher chlorinated PCDDs were also low. *See* Table 1. Like the ball clays, however, the U.S. kaolin contained low concentrations of all PCDFs.

Ferrario *et al.* confirmed our conclusion that a natural formation of PCDDs likely is the source of these compounds in ball clay (4, 8). Moreover, we received a copy of an unpublished 1992 study prepared by Environ Corporation for the China Clay Producers Association, Inc (9). In that study, kaolin and clay from 24 clay mines in Georgia were analyzed for PCDDs and PCDFs. All samples contained varying concentrations of PCDDs. Further, according to the China Clay Producers study, these PCDDs were formed at the time the strata were deposited and not by chemicals used in the mining processes. According to the China Clay Association, the kaolin and clay were formed 70 million years ago during the Cretaceous period (10).

We have determined the chemical composition of the four U.S. ball clay, the three U.S. kaolin, and the four newest German kaolin samples. Selected results for these samples are listed in Table 2. A preliminary evaluation of these data indicates similar elemental composition in U.S. ball clay and German kaolin. We are currently conducting an extensive study into the mechanism of formation of dioxins in the clays and kaolin.

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Table 1. PCDD and PCDF concentrations (ng/kg) in Ball Clay and Kaolin samples.

	US Ball Clay				**US Kaolin**			**German Kaolin**				
	1*	2*	3*	4*	1*	2*	3*	1*	2	3	4	5
2378 TCDF	<0.040	<0.048	0.066	<0.028	<0.028	<0.032	<0.024	0.042	0.052	<0.050	<0.040	<0.040
SUM TCDF	0.55	1.6	3.1	0.74	0.20	28	0.55	0.43	2.4	1.0	62	
2378 TCDD	43	100	240	20	<0.045	<0.058	<0.04	33	130	7.2	5.7	<0.060
SUM TCDD	520	3 600	2 800	1 300	2.1	840	18	350	4100	160	100	4.5
12378 PeCDF	<0.087	<0.088	0.11	0.094	0.069	<0.056	<0.045	0.078	0.043	<0.050	<0.050	<0.040
23478 PeCDF	0.15	<0.062	0.082	0.20	0.031	0.086	<0.029	<0.031	0.085	<0.050	0.15	<0.040
SUM PeCDF	0.67	1.4	2.0	0.67	0.19	6.1	0.095	0.3	1.3	0.34	0.33	
12378 PeCDD	330	660	700	270	0.21	<0.16	<0.15	85	220	10	5.6	0.64
SUM PeCDD	3 400	11 000	11 000	3 600	2.4	190	7.2	1 000	2 800	270	100	12
SUM HxCDF	2.4	5.5	3.9	1.2	0.22	1.3	0.11	0.6	0.18	0.27		0.11
123478 HxCDD	680	490	510	230	<0.06	<0.098	<0.085	56	36	11	4.8	1.1
123678 HxCDD	470	820	840	1 300	0.082	0.94	0.36	96	78	21	6.6	1.3
123789 HxCDD	1 200	2 500	1 800	1 200	0.25	0.76	0.60	320	240	84	25	4.4
SUM HxCDD	7 700	17 000	11 000	5 500	0.75	16	1.8	2100	2700	760	180	34
SUM HpCDF	1.1	10	0.68	2.5	0.052			0.36		0.40		
1234678 HpCDD	9 900	6 200	27 000	4 800	0.5	7.2	1.1	1200	600	370	160	31
SUM HpCDD	23 000	13 000	56 000	6 900	0.93	17	1.9	3200	2000	1100	420	97
OCDF	24	28	27	19	0.099	<0.082	<0.069	3.5	<1.5	1.2	<0.19	<0.21
OCDD	190 000	130 000	140 000	230 000	16	530	18	7 700	3 900	2 700	1 500	220
I-TEQ	730	1000	1 300	700	0.22	0.94	0.21	140	280	30	15	1.6
WHO-TEQ	720	1200	1 600	620	0.32	0.50	0.23	198	390	33	17	1.7

* Rappe, C., and Andersson, R., Organohalogen Compds., 46, 9-11 (2000) (7)

Table 2. Mineralology and Selected Elements (µg/g) from Ball Clays and Kaolin

	U.S. Ball Clay				U.S. Kaolin		
	1	2	3	4	1	2	3
Kaolinite	~60	~60	~60	~20	~95	~95	~95
Quartz	~40	~40	~40	~60	~5	~5	~5
Ångstrom lay (Type)	---	---	---	~20 (14)	---	---	---
agnesium	2977.80	3847.34	6735.74	32234.04	2448.43	610.09	1239.97
luminum	150435.95	41383.23	38791.58	05762.54	08579.56	98062.16	07371.50
anganese	17.30	32.44	114.27	707.10	23.58	16.75	14.43
elenium	2.97	3.32	3.96	1.53	1.00	0.70	0.03
alcium	1830.35	2100.06	3138.73	6472.53	3161.99	1259.47	2426.08
ron	9047.26	13814.07	19479.32	75603.91	8710.79	6683.79	9864.54
otassium	2516.06	1444.73	2977.94	6217.02	1273.40	2055.62	940.37
itanium	14887.96	11908.10	11994.67	6812.92	11068.13	2760.96	11338.69

	German Kaolin				
	1	2	3	4	5
Kaolinite	N/A	~20	~20	~20	~20
Quartz	N/A	~65	~50	~50	~50
Ångstrom lay (Type)	N/A	~15 (10)	~30 (10)	30 (10)	~30 (10)
agnesium	N/A	8538.32	12845.58	8054.84	9730.19
luminum	N/A	154513.68	151297.25	79236.72	68354.44
anganese	N/A	53.92	88.68	36.14	1169.05
elenium	N/A	2.89	4.66	12.15	1.31
alcium	N/A	5262.23	5487.63	1626.56	1548.16
ron	N/A	16921.36	19654.78	12084.87	52714.35
otassium	N/A	10579.22	13988.49	6627.50	6139.90
itanium	N/A	7462.21	9470.88	7166.27	6027.58

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