CONCENTRATIONS OF PCDDs IN BALL CLAY AND KAOLIN

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Introduction

From 1994-2000, we conducted an extensive study of PCDDs and PCDFs in the State of Mississippi, USA. Specifically, we analyzed approximately 300 samples, including soil, sediment, air, pine needles, sludge, wastewater effluent, food, farm-raised catfish, catfish feed, and catfish pond sediment. Our study found extraordinarily high octa- and heptaCDDs concentrations in sediment from the Leaf-Pascagoula River system and in man-made and naturally-formed lakes with no known anthropogenic source (1,2,3,4). A later part of our study similarly found high octa- and heptaCDDs concentrations in the soybean meal component of catfish feed (5). Moreover, 2,3,7,8-tetraCDD and 1,2,3,7,8-penta CDD concentrations of the catfish feed were unusually high. It was later determined by Ferrario et al., that ball clay added to the soybean meal was the source of the PCDDs (6), and that the ball clay also was used in chicken feed (6,7).

Ball clay is a fine-grained hydrated aluminium silicate with high organic content, good plasticity, and strong bonding power (7). The ball clay analyzed by US EPA was from a mine in Crenshaw, Mississippi. As noted above, the ball clay was added to the soybean meal component of the catfish and chicken feed. The ball clay was a minor component (<1%) of the catfish feed and chicken feed. US EPA supposedly stopped further distribution of contaminated soybean meal by the two manufacturers in Arkansas, USA (7). The feed containing the ball clay was retrieved from the catfish and chicken producers for disposal (7).

In this study, we analyzed four ball clay samples and four Kaolin samples for PCDDs and PCDFs. Kaolin and ball clay are similar in chemical composition.

Methods and materials

In August, 1999, we obtained from the producers four ball clay samples and three Kaolin samples. The ball clay samples were mined in Kentucky, U.S.A. The three Kaolin samples were mined in North Carolina and Georgia, U.S.A. In addition, we obtained one Kaolin sample from Germany. All samples were dissolved in 150 ml of toluene. The extracts were purified first in a multistep silica column, followed by a basic alumina column. The final step was made on a Carbopack/Celite column. The final extracts were evaporated and 30 µl of the internal standard was added to each. HRGC/HRMS analyses was performed on each sample with a 60 m JW DB-5 column directly attached to the VG instrument (70/70S).

Results and discussion

The ball clay results and the Kaolin results are summarized in Table 1. All ball clay samples had extraordinarily high concentrations of PCDDs. The mean for 2,3,7,8-tetraCDD in the four ball clay samples was 100 pg/g, and the highest concentration was 240 pg/g; the mean for 1,2,3,7,8-pentaCDD was 490 pg/g, and the highest concentration was 700 pg/g. The concentrations of all the other toxic congeners were similarly high: 1,2,3,4,7,8-hexaCDD (mean=478 pg/g, high=680 pg/g), 1,2,3,6,7,8-hexaCDD (mean=858 pg/g, high=1,300 pg/g); 1,2,3,7,8,9-hexaCDD (mean=1,675 pg/g, high=2,500 pg/g); 1,2,3,4,6,7,8-heptaCDD (mean=11,975 pg/g, high=27,000 pg/g); OCDD (mean=172,500 pg/g, high=230,000 pg/g). On the other hand, all 2,3,7,8-substituted CDFs in all four ball clay samples were extraordinarily low. In fact, 2,3,7,8-tetraCDF was detected in only one sample (at 0.066 pg/g) and 1,2,3,7,8-pentaCDF was detected in only two samples (at 0.11 pg/g). These PCDD concentrations are much higher than those reported by Hayward, et al., (7).

Notwithstanding the similarities in chemical composition with ball clay, all three U.S. Kaolin samples contained very low concentrations of all 2,3,7,8-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 CDDs were also extremely low, except for one Kaolin sample that had an OCDD concentration of 530 pg/g. See, Table 1. Like the ball clay, however, all Kaolin samples contained low concentrations of all PCDFs.

Inexplicably, the German Kaolin sample contained high concentrations of PCDDs like the ball clay (and unlike the U.S. Kaolin samples). See, Table 1.

The extraordinarily high PCDD concentrations in the ball clay and German kaolin samples confirms our earlier findings in farm-raised catfish (1,8), and catfish feed (5,8). These results also confirm our isolation of the source of these PCDDs to catfish feed, and in particular, the soybean meal component of such feed (5,8). Others confirmed our findings and determined that a ball clay added to the soybean meal was the source of PCDDs (6,7).

Our results here also confirm our earlier hypothesis of a natural formation of PCDDs in the ball clay and German Kaolin (5). This natural formation in ball clay has now been observed by others (6,7).

Although US FDA claimed to have stopped distribution of the soybean meal in 1997 (7), as noted above, we easily obtained ball clay samples from the producers in August 1999. Moreover, many people in the United States, especially pregnant women, actually eat raw clay and Kaolin, the exact substances we analyzed in this study (9).

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References

1.C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, S. E. Kulp and C. Lau. *Chemosphere* 34, 1297-1314 (1997).
2.C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, C. Lau and F. Howell. *Organohalogen Compds.* 32, 88-93 (1997).
3. C. Rappe, R. Andersson, K. Cooper, H. Fiedler, C. Lau, M. Bonner and F. Howell. *Organohalogen Compds.* 32, 18-22 (1997).
4.C. Rappe, S. Bergek, R. Andersson, K. Cooper, H. Fiedler, R. Bopp, F. Howell and M. Bonner. *Organohalogen Compds.* 43, 111-116 (1999).
5.C. Rappe, S. Bergek, H. Fiedler and K.R. Cooper. *Chemosphere.* 36, 2705-2720 (1998).
6.J. Ferrario, D. McDaniel and C. Byrne. *Organohalogen Compds.* 40, 95-99 (1999).
7.D.G. Hayward, D. Nortrup, A. Gardner and M. Clower, Jr. Env. Research Section A. 81, 248-256 (1999).
8.H. Fiedler, K. Cooper, S. Bergek, M. Hjelt, C. Rappe, M. Bonner, F. Howell, K. Willett and S. Safe. *Chemosphere.* 37, 1645-1656 (1998).
9.Swerdlow, Joel L., National Geographic, 197, 98-117 (April, 2000).

Table 1. PCDD and PCDF concentrations (pg/g) in Ball Clay and Kaolin samples.

	Ball Clay 1	Ball Clay 2	Ball Clay 3	Ball Clay 4	Kaolin 1	Kaolin 2	Kaolin 3	German Kaolin
2378 TCDF	<0.04	<0.048	0.066	<0.028	<0.028	<0.032	<0.024	0.042
SUM TCDF	0.55	1.6	3.1	0.74	0.20	28	0.55	0.43
2378 TCDD	43	100	240	20	<0.045	<0.058	<0.04	33
SUM TCDD	520	3600	2800	1300	2.1	840	18	350
12378 PeCDF	<0.087	<0.088	0.11	0.094	0.069	<0.056	<0.045	0.078
23478 PeCDF	0.15	<0.062	0.082	0.20	0.031	0.086	<0.029	<0.031
SUM PeCDF	0.67	1.4	2	0.67	0.19	6.1	0.095	0.3
12378 PeCDD	330	660	700	270	0.21	<0.16	<0.15	85
SUM PeCDD	3400	11000	11000	3600	2.4	190	7.2	1000
SUM HxCDF	2.4	5.5	3.9	1.2	0.22	1.3	0.11	0.6
123478 HxCDD	680	490	510	230	<0.06	<0.098	<0.085	56
123678 HxCDD	470	820	840	1300	0.082	0.94	0.36	96
123789 HxCDD	1200	2500	1800	1200	0.25	0.76	0.60	320
SUM HxCDD	7700	17000	11000	5500	0.75	16	1.8	2100
SUM HpCDF	1.1	10	0.68	2.5	0.052			0.36
1234678 HpCDD	9900	6200	27000	4800	0.5	7.2	1.1	1200
SUM HpCDD	23000	13000	56000	6900	0.93	17	1.9	3200
OCDF	24	28	27	19	0.099	<0.082	<0.069	3.5
OCDD	190000	130000	140000	230000	16	530	18	7700
I-TEQ	730	1000	1300	700	0.22	0.94	0.21	140
WHO-TEQ	720	1200	1600	620	0.32	0.50	0.23	198