An Assessment of Dioxin Levels in Processed Ball Clay from the United States

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Introduction

The presence of dioxin-like compounds in ball clay was discovered in 1996 as a result of an investigation to determine the sources of elevated levels of dioxin found in two chicken fat samples from a national survey of poultry [1]. The investigation indicated that soybean meal added to chicken feed was the source of dioxin contamination. Further investigation showed that the dioxin contamination came from the mixing of a natural clay known as "ball clay" with the soybean meal as an anti-caking agent [2,3]. The FDA subsequently discontinued the use of contaminated ball clay as an anti-caking agent in animal feeds [4]. The source of the dioxins found in ball clay has yet to be established. A comparison of the characteristic dioxin profile found in ball clay to those of known anthropogenic sources from the U.S.EPA Source Inventory has been undertaken, and none of those examined match the features found in the clays. These characteristic features together with the fact that the geologic formations in which the clays are found are ancient suggest a natural origin for the dioxins [2,5].

The plasticity of ball clays makes them an important commercial resource for a variety of commercial uses. The percentage of commercial uses of ball clay in 2000 included: 29% for floor and wall tile, 24% for sanitary ware, 10% pottery, and 37% for other industrial and commercial uses. The total mining of ball clay in the U.S. for 2003 was 1.12 million metric tons [6]. EPA is examining the potential for the environmental release of dioxins from the processing/use of ball clays and evaluating potential exposure pathways. Part of this overall effort and the subject of this study includes the analysis of dioxin levels found in commercially available ball clays commonly used in ceramic art studios.

Methods and Materials

Sampling Design.

A wide variety of ball clays are used in ceramic art studios. The three U.S. mining companies that supply the majority of the ball clay are Old Hickory Clay Co, HC Spinks Clay Co, and Kentucky-Tennessee Clay Co. The Internet sites for these companies list the specific ball clays recommended for art ware and pottery use. These lists were used to identify the U.S. ball clays that are currently being marketed for use in art studios. Lack of marketing data prevented statistically based sampling of these clays. Instead, a non-statistical approach was taken which targeted the

most commonly used ball clays. Four-art supply houses were selected which collectively sell 13 of the 32 ball clays. An independent ceramics expert was contacted to help confirm that the most commonly used ball clays were included among these thirteen. The thirteen ball clays are listed in Table 1. Six of the ball clays were ordered from more than one supplier resulting in a total of 21 samples. By using multiple suppliers and ensuring that the most commonly used clays were included, it was judged that this approach would provide a reasonable indication of typical dioxin levels present in ball clays used in art studios.

Fifty-pound bags of each of the clays were ordered from four different suppliers and delivered to the laboratory using commercial carriers. The samples were inspected to confirm their identity and to evaluate their condition. They were then given internal identification numbers, logged in, and stored at room temperature. Sub-samples were collected from each 50-pound bag for dioxin analyses, for total organic carbon analyses, and for the determination of specific gravity and bulk density. These measurements will be considered and utilized in the exposure assessment. Duplicate samples were collected from four randomly selected clays and included in the analysis. The identity of all the samples was unknown to the analysts for the remaining sample preparation and analyses.

Samples were prepared in sets of twelve consisting of a method blank, a fortified laboratory control sample, a duplicate and nine samples. The sample preparation and analytical procedures used were a modified version of EPA Method 1613: Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS [7]. Approximately five (5) grams of sample were accurately weighed, mixed with sodium sulfate, and introduced into a glass-fiber extraction thimble. They were then fortified with 200 picograms of ^{13}C labeled 2,3,7,8–chlorine substituted PCDD/F recovery surrogates and Soxhlet extracted with benzene for 24 hours. The extracts were solvent exchanged with hexane and “cleaned -up” with sequential acidified/basic silica gel**,** alumina, and PX-21 graphitized carbon. The cleaned-up extracts were then fortified with ^{13}C internal standards and analyzed on a Micromass Ultima operated in the lock mass drift correction mode at a resolution of 10,000.

Four blind duplicates were created during the preparation of sub-samples and demonstrated relative percent differences of 3.1, 3.7, 4.9, and 13.1%. Duplicates, fortified samples, recoveries of ^{13}C surrogates, method blanks, and other QA/QC elements were all within the limits as defined in the Quality Assurance Project Plan for this study.

Results and Discussion

Total organic carbon analyses were performed on all the samples utilizing EPA Method 415.1 [8]. The range for the samples was 0.06% to 1.1% with a median of 0.40% and geometric mean of 0.36%. In many types of environmental media, dioxin levels are correlated with organic carbon levels. However, in the clay samples analyzed, no correlation was observed. A plot of the total organic carbon levels vs. TEQ concentrations revealed that the data appear to be randomly scattered with a correlation coefficient of 0.0367.

All samples were measured for bulk and particle density and found to be very uniform. Bulk density ranged from 0.56 to 0.87 g/cm^3 with an average of 0.73

g/cm^3. Particle density ranged from 2.59 to 2.68 g/cm^3 with an average of 2.64 g/cm^3.

A summary of the results of the analyses is presented in Table 2. The chlorinated furan congener concentrations in all the samples were less than a 1.0 ppt for all the congeners except 1,2,3,4,6,7,8-HpCDF, which ranged from 1 to 5 ppt, and OCDF, which ranged from 5 to 80 ppt. These relatively low concentrations of the chlorinated furans in the presence of elevated levels of the chlorinated dioxins are a commonly observed feature of ball clay. Their contributions to the TEQ were less than 0.07% in all the samples and are not further discussed.

The dioxin congener profile has the following characteristics:

- The dominant congener is OCDD, followed by 1,2,3,4,6,7,8-HpCDD.
- Among the toxic hexa-dioxins, the 1,2,3,7,8,9-HxCDD is the dominant congener, followed by the 1,2,3,6,7,8-HxCDD, and then by the 1,2,3,4,7,8-HxCDD.
- The concentration of 1,2,3,7,8- PeCDD exceeds the 2,3,7,8-TCDD concentration.

These same profile characteristics have been observed in other analyses of processed ball clays [2]. The average WHO-TEQ for the entire set of 21 samples was 808 ppt with a range from a low of 289 to a high of 1470 ppt TEQ and a median value of 771 ppt TEQ. On a TEQ basis, the samples were distributed as follows: four were between 289 and 500 ppt, eleven were between 500 and 1000 ppt, and six were between 1000 and 1500 ppt. 1,2,3,7,8-PeCDD was the largest contributor to the total TEQ at an average value of 46%. The other major contributors to the total TEQ were the 1,2,3,7,8,9-HxCDD at 18%, followed by the 1,2,3,4,6,7,8-HpCDD at 12%. These features are characteristic of all the processed ball clay samples analyzed in this study and are remarkably similar to those described previously [2] where the relative contribution of the penta-, hexa-, and hepta congeners to the TEQ were 44, 21, and 14 %, respectively, when compared to 46, 18, and 12% from this study.

It is interesting to note that Hosseinpour et al. [9] have theorized that the addition of water (20%, w/w) to ball clay prior to extraction results in the deactivation and widening of the silica layers, making the PCDDs more available for extraction. They compared the efficiency of Soxhlet extraction with toluene to accelerated solvent extraction using toluene after hydration and concluded that the hydration of the clay resulted in a WHO TEQ-PCDD/F level 2.5 times higher than the Soxhlet method. In this study the classical Soxhlet extraction using benzene was employed in order to be consistent with our previous work with ball clay. Studies are presently being conducted to further evaluate the effect of hydration on the dioxin levels reported for ball clay.

The results presented here provide a range of dioxin levels across ball clays in general. The lack of marketing data and limited sampling precluded a definitive determination characterizing the dioxin concentration of any particular type of ball clay analyzed in this study.

This study was conducted to support EPA efforts to evaluate the potential for environmental release of dioxins from the processing/use of ball clays and evaluating potential exposure pathways. Observations from this study specific to these issues are discussed below:

- This study has found that the average dioxin level in processed ball clay is over 100 times greater than average level identified in the September 2000 EPA Draft Assessment for rural background soils (2.5 ppt TEQ) [10]. Human exposure may occur during the handling and use of these clays. This could include individuals involved in packaging/shipping, workers in the ceramic industry and artists/hobbyists who use ball clays. Potential exposure pathways include dermal contact, inhalation of airborne dusts, and inadvertent ingestion. EPA currently has a project underway to evaluate exposures in ceramic art studios.
- Ferrario et al. [2] observed that in raw ball clay the concentration of 2,3,7,8-TCDD exceeds 1,2,3,7,8- PeCDD, and the opposite is seen in processed clays. In this study, all processed ball clay samples also showed lower levels of 2,3,7,8-TCDD than 1,2,3,7,8-PeCDD. The mechanisms of congener loss/formation that would result in this profile change remain to be firmly established. However, this congener shift could indicate that dioxin releases are occurring during the initial processing of raw ball clay, which involves hot air drying and grinding operations. EPA currently has a project underway measuring emissions at clay processing operations.
- A previous investigation[3] compared dioxin levels in processed ball clay and fired ceramic products made from the same type of clay. Much lower dioxin levels were found in the final products and it was speculated that these losses could mean that either releases were occurring during the manufacturing process or destroyed in the firing process. This study confirms that elevated dioxin levels are commonly found in commercially processed ball clays. EPA plans stack testing at a commercial ceramic manufacturer to better understand the magnitude of these potential releases.

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Disclaimer: This paper reflects the views of the authors and does not necessarily reflect the views of the Environmental Protection Agency and no official endorsement should be inferred. The mention of trade names or commercial products constitutes neither an endorsement nor a recommendation of use.

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Table 1. Selected Clays

Company	Product Name	Number of Samples
Old Hickory	Taylor	1
	Thomas	2
	No. 5	1
HC Spinks	C & C	1
	New Foundry Hill Crème	2
Kentucky Tennessee	Bell Dark	1
	Jackson	1
	KT#1-4	1
	KTS-2	1
	Tennessee #5	2
	Kentucky Stone	2
	Old Mine #4	4
	XX Sagger	2

Table 2. Summary of Results from the Analysis of Ball Clay (pg/g)

	Avg	StdDev	RSD	Median	Min	Max	WHO-TEF	TEQ
PCDFs								
2,3,7,8-TCDF	ND	-	-	ND	ND	ND	0.10	0.00
1,2,3,7,8-PeCDF	0.03	0.10	333	ND	ND	0.41	0.05	0.00
2,3,4,7,8-PeCDF	0.12	0.20	170	ND	ND	0.56	0.50	0.06
1,2,3,4,7,8-HxCDF	0.45	0.41	93	0.44	ND	1.62	0.10	0.04
1,2,3,6,7,8-HxCDF	0.19	0.29	156	0.00	ND	1.07	0.10	0.02
2,3,4,6,7,8-HxCDF	0.42	0.35	84	0.46	ND	1.03	0.10	0.04
1,2,3,7,8,9-HxCDF	ND	-	-	ND	ND	ND	0.10	0.00
1,2,3,4,6,7,8-HpCDF	1.98	1.11	56	1.58	0.89	5.47	0.01	0.02
1,2,3,4,7,8,9-HpCDF	0.38	0.38	100	0.38	ND	0.99	0.01	0.00
OCDF	32	21	65	21.9	10.6	78.2	0.0001	0.00
PCDDs								
2,3,7,8-TCDD	76	60	79	63.5	21.8	291	1	76.0
1,2,3,7,8-PeCDD	374	144	38	387	125	588	1	374
1,2,3,4,7,8-HxCDD	335	141	42	313	142	636	0.10	33.5
1,2,3,6,7,8-HxCDD	526	204	39	523	167	944	0.10	52.6
1,2,3,7,8,9-HxCDD	1480	608	41	1570	394	2550	0.10	148
1,2,3,4,6,7,8-HpCDD	9780	4480	46	8600	3940	19500	0.01	97.8
OCDD	254000	88200	35	233000	118000	471000	0.0001	25.4
Total								
TCDF	1.49	0.99	67	1.12	0.35	3.45		
TCDD	1450	606	42	1600	412	2370		
PeCDF	3.10	2.03	66	2.41	0.00	7.69		
PeCDD	4600	1890	41	4880	1560	7140		
HxCDF	7.41	3.87	52	6.53	1.94	16.3		
HxCDD	13500	5710	42	12800	4800	21900		
HpCDF	12.1	5.96	49	11.2	3.75	27.9		
HpCDD	25000	11700	47	24400	9320	44900		
Summary TEQs	808	318	39	771	289	1470		808

ND (Not detected; LOD = 0.1 ppt)