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Concentrations of polychlorinated dibenzo-*p*-dioxins in processed ball clay from the United States

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Abstract

Processed ball clays commonly used by the ceramic art industry in the United States were collected from retail suppliers and analyzed for the presence and concentration of the 2,3,7,8-Cl substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs). The average PCDD toxic equivalent (TEQ) concentrations of these processed ball clays was approximately 800 pg/g (TEQ–WHO) with characteristic congener profiles and isomer distributions similar to patterns of previously analyzed raw and processed ball clays. The PCDF concentrations were below the average limit of detection (LOD) of 0.5 pg/g. Correlation analyses reveal no significant relationship between total organic carbon (TOC) and either individual, homologues, and total tetra-through octa-chlorinated PCDD congeners, or TEQ concentrations of the processed ball clays. The results are consistent with earlier studies on levels of PCDDs in ball clays. Data from earlier studies indicated that dioxins may be released to the environment during the processing of raw clay or the firing process used in commercial ceramic facilities. The presence of dioxin in the clays also raises concerns about potential occupational exposure for individuals involved in the mining/processing of ball clay, ceramics manufacturing and ceramic artwork.

Keywords: Pottery; Dioxins; Ceramics; Human exposure; Ball clay; Congener profile

1. Introduction

The presence of dioxin 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 (Ferrario et al., 1997). The investigation indicated that the chickens were exposed through their feed from the soybean meal added to the chicken feed. Further investigation showed that the dioxin contamination originated from the mixing of natural clay known as "ball clay" with the soybean meal as an anti-caking agent (Ferrario et al., 2000; Ferrario and Byrne, 2002). The United States Food and Drug Administration (FDA) subsequently discontinued the use of contaminated ball clay as an anti-caking agent in animal feeds (Food and Drug Administration, 2000). 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 USEPA source inventory has been undertaken, and none of those examined match the features found in the clays. Many of the samples have been collected from undisturbed ancient geologic formations. It seems unlikely that human activity could have contaminated these deposits without disturbing them. Accordingly, several investigators have supported the theory of a natural origin for the dioxins (Rappe et al., 1999; Ferrario et al., 2000; Gadomski et al., 2003). Gaus et al. (2002), however, has proposed the hypothesis that chlorinated phenols are sufficiently mobile to have diffused into these formations since their

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introduction in the mid-nineteen hundreds and undergone natural transformations to produce the current profiles.

Ball clay is an important industrial 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 US for 2003 was 1.12 million metric tons (US Geological Survey, 2004). Due to its strength, plasticity, and fast casting properties, ball clay is a vital component in ceramic applications, which include sanitary ware, dinnerware, ceramic tiles, and artwork, and non-ceramic applications, which include fillers and extenders in polymers, adhesives, plastics, sealants, fertilizers, and insecticides.

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 include the analysis of dioxin levels found in commercially available ball clays commonly used in ceramic art studios.

2. Experimental section

2.1. Sampling design

A wide variety of ball clays are used in ceramic art studios. The three US 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 US 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 systematic approach would provide a reasonable indication of typical dioxin levels present in ball clays used in art studios.

Table 1
Selected processed ball clays

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

2.2. Materials

Twenty-three kilogram 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. Subsamples were collected from each bag for dioxin analyses, for total organic carbon analyses, and for the determination of specific gravity and bulk density. These measure- ments 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.

2.3. Analysis

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 (USEPA, 1994). Approximately 5 g of sample were accurately weighed, mixed with sodium sulfate, and introduced into a glass–fiber extraction thimble. They were then fortified with a solution containing 200 pg each of fifteen ^{13}C labeled 2,3,7,8-chlorine substituted PCDD/F recovery surrogates and Soxhlet extracted with benzene for 24 h. 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 two ^{13}C internal standards (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) 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.

In addition, total organic carbon analyses were performed on all samples utilizing EPA Method 415.1 (USEPA, 1979). Bulk and particle density measurements were performed in accordance with ASTM C29 ASTM