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Serum concentrations of polychlorinated dibenzo-*p*-dioxins among ceramicists

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HIGHLIGHTS

- First measurements of serum dioxin levels in ceramicists.
- Some evidence of elevated dioxin levels relative to background.
- Measured levels not inconsistent with calculated levels reported in earlier study.

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) occur naturally in ball clay at elevated concentrations. Thus, persons who habitually work with clay may be at risk for exposure to PCDDs. An earlier case report provided some evidence of elevated PCDD levels in serum for long-term hobby ceramicists; however, no previous study has measured serum dioxin concentrations among ceramicists. This study measured PCDD serum levels for 27 individuals involved in ceramics making. The average residual, defined as the average of the [log measured serum lipid concentration – log background serum lipid concentration], was calculated and then tested to determine whether it was significantly different from zero. The *p*-values for the average residuals indicated that the serum lipid concentrations for several PCDD congeners were elevated relative to background. The number of significant residuals increased dramatically if the background concentrations were adjusted to account for the fact that they were not contemporaneous with the measurements for the ceramicists. The ratio of the 1,2,3,6,7,8-HxCDD concentration to the 1,2,3,7,8,9-HxCDD concentration was greater than 1.0, unlike in ball clay, suggesting that although long-term working with ball clay elevates the PCDD levels in serum somewhat, it is not the predominant source of the PCDD body burden for ceramicists.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) have been identified as naturally occurring in ball clay (Ferrario et al., 2000; Holmstrand et al., 2006; Schmitz et al., 2011). PCDDs dominate the dioxin content in ball clay, with Schmitz et al. (2011) reporting an average concentration of 98200 pg g^{-1} for PCDDs versus 15 pg g^{-1} for PCDFs. An analysis of kaolin clay samples from around the world suggested that the ball clays mined in the United States have particularly high concentrations of PCDDs (Horii et al., 2011), with an average toxic equivalent (TEQ) of 1600 pg g^{-1} for the samples analyzed, orders of magnitude higher than the samples from other countries. About 900000 metric tons of ball clay were produced in the United States in 2012. Of this, about 58% was used in the manufacture of tile and dishware (U.S. Geological Survey, 2013). A survey conducted by the National Endowment for the Arts estimated that as many as 11.8 million adults may have contact with ball clay through recreational activities (National Endowment for the Arts, 2013) and another 22000 adults are employed in pottery and ceramics manufacturing (U.S. Dept. of Labor, 2010). Considering that ball clay is a common component of ceramic clay (typically in the range of 20%) (U.S. EPA, 2008), both vocational and professional ceramicists may be potentially exposed to high concentrations of PCDDs regularly.

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The individual with the highest lipid-adjusted serum TEQ in the University of Michigan Dioxin Exposure Study (UMDES) had a TEQ (based on the 29 compounds assigned toxic equivalency factors (TEFs) by the World Health Organization (Van den Berg et al., 2006)) of 211 pg g^{-1} (>2.5 studentized residuals above the mean of 946 subjects, after adjusting for age, age^2 and body-mass index) (Franzblau et al., 2008), dominated by PCDDs as in ball clay (Ferrario et al., 2000; Holmstrand et al., 2006; Horii et al., 2011; Schmitz et al., 2011). This person had been a hobby ceramicist for over 30 years, working with clay in her home and firing it in her basement (Franzblau et al., 2008). It was thought that perhaps that exposure to ball clay was responsible for the significantly higher TEQ in this individual's blood, given the lack of other potential contributing factors (such as occupation) and the dominance of her serum's TEQ by PCDDs. To assess the possibility of exposure of hobby ceramicists via inhalation during the process of ceramics firing, another study was conducted in which air samples were taken around a kiln in an art studio (Broadwater et al., 2014). Although the ball clay that was fired contained an appreciable quantity of dioxins (mean TEQ based on PCDDs was 1370 pg g^{-1}) and the fired clay contained essentially none (mean TEQ based on PCDDs was 0.62 pg g^{-1}), insignificant air-borne concentrations were detected around the kiln during firing even in the absence of ventilation (Broadwater et al., 2014). Thus, it appeared that the dioxin content of the clay was destroyed during firing and fugitive emissions were minimal. However, this study did not evaluate the possibility of exposure of ceramicists through other routes.

The U.S. EPA conducted a study estimating inhalation, dermal contact, and incidental ingestion for ten subjects working with clay in an art studio (U.S. EPA, 2008). This study estimated the exposure based on measurements of clay particulates in air, residues on skin and deposition on media representing food and beverages, utilizing dioxin concentrations in clay reported in the literature. The mean exposure was calculated to be about 4% of the typical dose of the general adult population of 0.65 pg TEQ $kg^{-1}day^{-1}$ (or 45 pg TEQ day^{-1} for a 70-kg adult) (Lorber, 2002), with a high of about 18%, and occurred principally through dermal contact. However, this study did not measure dioxins in the clay used or in the serum of the subjects. Ferrario et al. (2007) pointed out that there have been a number of epidemiological studies of workers in clay pottery industries looking at possible exposure to polycyclic aromatic hydrocarbons (PAHs), but aside from the case report noted above (Franzblau et al., 2008), no study has measured serum dioxin concentrations among ceramicists. This study was undertaken to evaluate whether prolonged contact with ball clay mixtures typically used by ceramicists impacts serum PCDD concentrations. Characterizing the potential magnitude of dioxin exposure that occurs when working with ball clay is critical to understanding the level of risk involved in the making of ceramics.

2. Methods

2.1. Subject recruitment

Participants from two groups in Southeast Michigan were recruited for this study. One set of participants was recruited from a local clay production and tile-making facility through an informational meeting at the production facility. All employees were invited to participate in the study, provided they satisfied eligibility constraints based on American Red Cross (ARC) blood donation requirements, which dictate that an individual must not be taking blood thinners, must be free of blood disorders and must weigh more than 110 lb (ARC, 2013). A total of 14 participants were recruited in this manner.

In addition to the group from the tile-making facility, 13 long-term art ceramicists who also satisfied ARC blood donation requirements, were recruited for the study through their involvement with a regional ceramic arts association. Most of these individuals were educators and had regular contact with ball clay both vocationally and professionally. Demographics of the 27 participants, including age, body-mass index (BMI) and gender, are presented in Table 1.

2.2. Questionnaire

All of the participants answered a questionnaire created for this study, modified from that used in the University of Michigan Dioxin Exposure Study (UMDES) (Garabrant et al., 2009a,b). Questions retained from the UMDES covered topics that had been found to yield statistically significant predictors of serum dioxin concentrations, including diet, job history, education, smoking, childbearing, age and other demographic information (Garabrant et al., 2009b). Additional questions pertaining to clay practices based upon discussions with an experienced ceramicist were added in order to permit exploration of which clay activities may influence serum dioxin concentrations. These questions asked about length of time working with clay, frequency of working with clay, types of clay used, types of activities with clay, firing practices, personal hygiene and use of personal protective equipment while working with clay.

2.3. Blood collection and serum analysis

In addition to self-administering the questionnaire described above, each participant donated a 40-mL whole blood sample, collected by an experienced phlebotomist at the participant's workplace or in a University of Michigan facility in May to June of 2012. Samples were put on wet ice and immediately processed for shipment. The blood samples were allowed to clot, after which they were centrifuged. The serum was decanted and frozen at −20 °C. Data on the quantity of serum that was obtained from the study subjects are given in Table 2. The frozen serum samples were sent to Vista Analytical Laboratory (El Dorado Hills, CA) where they were analyzed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using U.S. EPA method 8290 for the seventeen PCDF and PCDD congeners assigned TEFs by the World Health Organization (Van den Berg et al., 2006). The samples were weighed and spiked with isotopically-labelled internal standards, followed by exhaustive extraction with hexane. The extracts were then cleaned by passing them over silica gel, acid alumina and Florisil columns, after which they were transferred to a vial containing a recovery standard and tetradecane for HRGC/HRMS analysis. An initial calibration curve was analyzed to confirm the linearity of the instrument over the calibration range and was verified with a continuing calibration verification standard. Limits of detection (LOD) were sample and congener specific, and were defined as 2.5 times the instrument noise level.

Each analytical sequence consisted of the serum sample, a lab method blank, an ongoing precision and recovery sample, two solvent blanks and two calibration standard solutions. The concentration of each analyte was calculated based on a standard linear calibration specific to each congener. The lipid content of the serum was determined using a UniCel DxC 600 (Beckman Coulter, Brea, CA), and Phillips formula, summing triglycerides and total cholesterol, was used to calculate the total serum lipids. Statistics on the percent lipid measured in the serum samples are given in Table 2. Concentrations are reported as lipid-adjusted (pg g^{-1} serum lipid). The protocol used here is the same as that followed in the UMDES study (Garabrant et al. (2009a).

Since a key signature of ball clay is the virtual absence of PCDFs relative to PCDDs (see data in, for example, Schmitz et al. (2011)),