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Evaluation of the release of dioxins and PCBs during kiln-firing of ball clay

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HIGHLIGHTS

- Air concentrations of dioxins did not increase during firing of contaminated, dry clay.
- Kiln-fired ball clay does not contain an appreciable amount of dioxins.
- Inhalation during firing of dry ball clay is an unlikely source of dioxin exposure.
- The temperature ramping up process did not cause dioxins to volatilize and escape.

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ABSTRACT

Ball clay is known to be naturally contaminated with high levels of polychlorinated di-benzo-*p*-dioxins (PCDDs). This study evaluated the potential for PCDD, polychlorinated dibenzofuran (PCDF) and polychlorinated biphenyl (PCB) release during the kiln firing of ball clay in an art studio. Toxic equivalence (TEQ) were calculated using World Health Organization (WHO) 2005 toxic equivalence factors (TEF) and congener concentrations. Ten bags of commercial ball clay were found to have an average TEQ of 1370 nanograms/kilogram (ng kg^{-1}) dry weight (dw), almost exclusively due to PCDDs (99.98% of TEQ). After firing, none of the 29 dioxin-like analytes was measured above the limits of detection (LOD) in the clay samples. Air samples were taken during firings using both low-flow and high-flow air samplers. Few low-flow air samples contained measurable levels of dioxin congeners above the LOD. The mean TEQ in the high volume air samples ranged from 0.07 pg m^{-3} to 0.21 pg m^{-3} when firing ball clay, and was 0.11 pg m^{-3} when no clay was fired. These concentrations are within the range measured in typical residences and well-controlled industrial settings. The congener profiles in the high-flow air samples differed from the unfired clay; the air samples had a considerable contribution to the TEQ from PCDFs and PCBs. Given that the TEQs of all air samples were very low and the profiles differed from the unfired clay, it is likely that the PCDDs in dry ball clay were destroyed during kiln firing. These results suggest that inhalation of volatilized dioxins during kiln firing of dry ball clay is an unlikely source of exposure for vocational and art ceramicists.

1. Introduction

Because of human health concerns and their persistence in the environment, PCDDs, PCDFs and PCBs have been subjected to intense scrutiny to delineate human exposure pathways. Historically, PCDDs and PCDFs were thought to be pyrogenic, primarily produced as byproducts of combustion processes. However, during an investigation into elevated PCDD concentrations in poultry, it was discovered that ball clay, used as an anti-caking ingredient in chicken feed, contained high levels of PCDDs (Ferrario and Byrne, 2000). Subsequent measurements have found that raw ball clay can have significantly elevated concentrations of these compounds as Ferrario et al. reported an average of 1510 ng kg^{-1} TEQ in clay from the Mississippi Embayment (which extends over approximately 116500 km^2 and covers parts of Mississippi, Kentucky and Tennessee), and an average of 808 ng kg^{-1} TEQ for ball clays available through retail outlets (Ferrario et al., 2000, 2007). The majority of the TEQ in ball clay is attributed to 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,7,8,9-HxCDD and 1,2,3,4 6,7,8-HpCDD, with a notable absence of contribution from the furans (Ferrario et al.,

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2007). Contamination of soils and sediments via anthropogenic sources does not exhibit such marked domination by PCDDs; thus, the profile of dioxins in ball clay suggests a natural origin (Ferrario et al., 2000; Holmstrand et al., 2006). Details of the geologic mechanism of dioxin production remain unknown, although evidence points to surface-promoted abiotic reactions associated with clay minerals (Holmstrand et al., 2006; Horii et al., 2008).

In 2010, about 910 000 metric tons of ball clay were produced in the United States. Of this, about 58% was used in the manufacture of tile and dishware (U.S. Geological Survey, 2011). Based on a National Endowment for the Arts survey, it was estimated that as many as 13.4 million adults in the US may have contact with ball clay through recreational work with clay (National Endowment for the Arts, 2009). Currently, there are no estimates of the number of children engaged in classroom or recreational ceramics activity, but clay work remains a common activity for this age group. Because of the existence of high concentrations of PCDDs in ball clay and the number of individuals who may come into contact with it, the possibility exists for significant human exposure from this source.

To evaluate possible exposure to dioxins in ball clay, the EPA conducted a study estimating inhalation, incidental ingestion and dermal contact for ten subjects engaged in ceramics activities in an art studio (U.S. EPA, 2008). The estimates of exposure were based on measuring levels of clay particulates in air, clay residues on skin and clay deposition on media representing food. However no dioxin measurements were made. Based on an average intake of 45 pg TEQ day^{-1} for a 70-kg adult, the estimated mean daily exposure from ceramics work was about 4% of the typical dose for the general adult population (Lorber, 2002). The EPA study did not attempt to address the potential for inhalation exposure during the firing of ceramic in kilns, but solely during tasks such as clay handling, mixing, sculpting and molding.

The University of Michigan Dioxin Exposure Study (UMDES) documented that the person with the highest lipid-adjusted serum TEQ in a sample of 946 persons from Michigan had a TEQ of 211 ng kg^{-1} (>2.5 studentized residuals above the mean after adjusting for age, age^2 and body-mass index). (In the UMDES and this study, serum TEQs included the sum of the contribution of all 29 PCDD, PCDF and dioxin-like PCB congeners given TEFs by the World Health Organization.) This individual had been a hobby ceramicist for 30 years, working with ball clay and firing it in unvented kilns in her basement (Franzblau et al., 2008). It was concluded that exposure to ball clay could be the primary source of the dioxins in her serum.

There has been limited investigation into the fate of dioxins in ball clay during the production of ceramics. The United Nations Environmental Programme acknowledges that kaolinitic and ball clay sites contribute PCDDs and PCDFs to the global dioxin inventory (UNEP, 2005). However, the contributions from contaminated sites and clay operations, such as mining and ceramic firing, are not included in the UNEP toolkit, possibly due to a paucity of emissions data. Comparative measurements made by Ferrario and Byrne of processed ball clay and fired ceramics showed no dioxins were left (concentrations below the limit of detection of 0.2 ppt for 2,3,7,8-TCDD) after a single firing at 1200 °C (Ferrario and Byrne, 2002). Concentrations of all dioxins can be reduced to very low levels with prolonged exposure to temperatures over 400 °C due to volatilization, and at temperatures of 977 °C, 99.99% destruction will occur (Shaub and Tsang, 1983; Lundin and Marklund, 2005). Thus, kiln temperatures at which typical firing takes place, at about 1000 °C or higher, are high enough to destroy these compounds. Temperatures must reach this critical point to provoke the necessary permanent physical changes in the clay body, but can reach temperatures as high at 1400 °C depending on the material being fired. However, as Ferrario and Byrne point out, the firing process involves a gradual ramp-up of the temperature and it is unknown whether these compounds volatilize and escape prior to the clay reaching a temperature at which these compounds are destroyed (Ferrario and Byrne, 2002). The EPA stated that "even though these high temperatures exist, it is unclear whether some release occurs," and has classified this source as category "E", implying that insufficient evidence is available to even make a preliminary estimate of release to the environment (U.S. EPA, 2004).

Given the possibility of a significant fraction of dioxins being released during the firing process, the size of population that might be exposed, and the documented case of an individual with a serum level consistent with high exposure to dioxins from clay, the process of ceramics production needs to be assessed for the potential release of dioxins to the environment. This study sought to quantify the discharge of dioxins during small-scale batch kiln firing of ball clay to evaluate this as a potential source of human exposure.

2. Methods

2.1. Clay firing

Ten 22.7 kg (50-lb) bags of dry, powder-form ball clay were obtained from a single source (Old Mine #4; Kentucky-Tennessee Clay Company, Mayfield, KY, USA); this clay is one of the most commonly used ball clays for art ceramicists. (Ferrario et al., 2007) Between 1140 and 1360 kg (2500–3000 lbs) of ball clay are used annually in the University of Michigan ceramics studio. Four bags of non-ball clay were also obtained for analysis (Hawthorne Bond #35 Fire Clay, Christy Minerals, High Hill, MO, USA). About 100 g of dry clay were collected from each bag (total of 14 samples) and submitted for chemical analysis.

Seven bags of ball clay were fired dry in the Ceramics Studio of the School of Art and Design at the University of Michigan; during each sampling period one 22.7 kg bag was fired. Typically, ball clay is mixed with non-ball clay in order to produce ceramics; ball clay proportions in the final mixtures range from 0% to 100%, with an average of 20% (U.S. EPA, 2008). Thus, firing 100% ball clay represents a potentially higher exposure situation. Each bag was fired individually in a fully programmable electric kiln (Automatic Kiln KM-1627PK, Skutt, Portland, OR, USA) in which temperatures were strictly controlled in order to mimic the typical process of ceramic formation. A professional ceramicist was consulted in order to ensure that the firing program chosen was a standard firing operating protocol that is widely used amongst ceramicists. Starting at ambient conditions, the temperature in the kiln was programmed to climb linearly up to 980 °C over a 12-h period. After achieving the desired temperature, the kiln shut off and then cooled back to room temperature. Two pyrometric cones were placed inside the kiln to ensure that the desired temperature was reached but not exceeded. The firing cone was O7, with a deformation temperature of 984 °C (1803 °F), while O6 was the guard cone, with a deformation temperature of 999 °C (1830 °F); after each firing was completed, the cones were visually inspected, confirming that the targeted temperature range had been achieved. Samples of about 100 g each were taken after two of the ball clay firing events and analyzed for dioxin content.

2.2. Air sampling

Initially, low flow air sampling (between 4 and 5 liters per minute) was conducted. The censorship proportion of these data was between 84% and 96%. These data and resulting discussion are presented in the accompanying supplement and will not be discussed further. Due to the high proportion of non-detects during low flow air sampling, five firing samples and one background