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VERTICAL DISTRIBUTION OF PCDDs IN A CLAY CORE FROM KENTUCKY, USA

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Introduction

Studies have found elevated levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) in ball clay and kaolin samples from specific regions in the United States and Germany [1, 2, 3]. In general, the congener profiles associated with these clay samples include, increasing PCDD concentration with increasing chlorine substitution, and low or even undetectable levels of PCDFs at comparable detection limits. Moreover, 1,2,3,7,8,9-HxCDD dominates the 2,3,7,8-substituted HxCDD isomers. The congener patterns and the high ∑PCDDs/ ∑PCDFs ratio associated with these samples are unlike those from known anthropogenic sources, chemical products or environmental samples. The natural processes that produce the PCDDs observed in these clay samples are not yet understood.

In 2000, Ferrario *et al*., reported results from the analysis of eight raw, and four processed ball clay samples from Sledge, Mississippi [1]. Each raw ball clay sample was dominated by OCDD followed by 1,2,3,4,6,7,8-HpCDD or, in two cases, 1,2,3,7,8,9-HxCDD. 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were found at extraordinarily high levels in the raw ball clay samples, with averages of 711 and 508 ppt dry weight (dw), respectively. Average PCDF values were lower than what was reported for an urban background sample, indicating the clear dominance of PCDDs. The authors suggested that a systematic evaluation of the dioxins in these clay deposits may provide information needed to develop a testable hypothesis to explain the possible natural origin of these compounds [1].

Later, Rappe *et al*., reported PCDD/F results from the analysis of US and German kaolin samples and US ball clay samples [3]. The data from the study indicated that the German kaolin and US ball clay both contained high PCDD concentrations and low or undetectable levels of PCDFs. In addition, the tetra-, penta- and hexaCDD patterns were similar in both the US ball clay and German kaolin. Although the patterns were similar, the relative concentrations were much higher in the US ball clay. The mean WHO-TEQ of the German kaolin was 128 pg/g, whereas the mean of the US ball clay samples was 1035 pg WHO-TEQ/g dm. This study demonstrated that the distinct non-anthropogenic pattern in ball clays and kaolin is not limited to the southern United States [3].

This distinct "natural formation" pattern observed in ball clay and kaolin samples from different regions of the world were from individual "grab" samples and not from contiguous samples collected from the same core. In the present study, we report PCDD/F results from the analyses of eight samples from one clay core from Kentucky.

Methods and Materials

Sampling

The clay core was obtained from a Kentucky mine (N36^0 52', W88^0 53') in August 2002. It was drilled without using any water or lubricants. The core was stored at the University of Notre Dame until October 2002, at which time eight samples were identified and prepared. Sampling of the core began at what corresponds to 10.1 meters below ground surface (BGS) and continued throughout the length of the core. The samples were taken at 10.1, 11.3, 12.5, 14.3, 15.8, 16.2, 17.7, and 18.9 meters BGS, and labeled C1-C8, respectively. All samples were sent to Umeå University for analysis.

Analysis

Each sample was homogenized before extraction. Seventeen internal standards were added to each sample and each sample was then Soxhlet-extracted for 15 hours in 150 mL of toluene. The extracts were first purified in a multistep silica column followed by a basic alumina column. The final step in the clean-up was made on a Carbon AX/21 Celite column. The final extracts were evaporated in 30 µL of tetradecane. Sample analysis was performed using HRGC/HRMS with a 60 m JW DB-5 column directly attached to a VG instrument (70/70S).

Results

Results from the 2,3,7,8-substituted PCDD/F analyses of the 8 core samples are shown in Figure 1. OCDD dominated each sample, followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD. OCDD concentrations range from 6,200 (C8) to 68,000 pg/g dw (C2), which correspond to samples collected from 18.9 and 11.3 meters BGS, respectively. The 1,2,3,4,6,7,8-HpCDD isomer is found in higher concentrations, ranging between 1.2 and 2.6 times greater than 1,2,3,4,6,7,9-HpCDD. Not surprisingly, 1,2,3,7,8,9-HxCDD had the highest concentrations among the toxic HxCDD isomers. The mean and median ratios between 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD are 1.53 and 1.46, respectively. 2,3,7,8,-TCDD concentrations ranged from 8-53 pg/g dw and 1,2,3,7,8-PeCDD concentrations ranged from 63-960 pg/g dw. The mean and median concentrations of 1,2,3,7,8-PeCDD are 414 and 385 pg/g dw, respectively. PCDFs were only detected in two of the samples (C1 and C4) at extremely low concentrations, and non-detects were set to zero in Figure 1.

Percent contribution of each PCDD homologue group to the ∑PCDDs along the depth of the core is illustrated in Figure 2. Figure 2 clearly shows that the contribution from each PCDD homologue group is similar throughout the length of the core. Contribution of the TCDDs range from 2.2-4.1, PeCDDs 4.6-7.9, HxCDDs 14-22, HpCDDs 27-32, and OCDD from 38-51%.

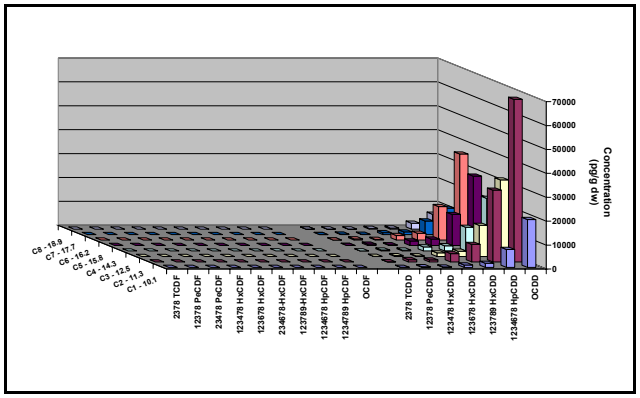

Figure 1. 2,3,7,8-Substituted PCDD/F concentrations along the depth of the core (meters BGS). Extremely low levels of PCDFs were detected at C1 and C4, ranging from 1.3 to 6.6 pg/g dw for 1,2,3,4,6,7,8-HpCDF and OCDF. PCDF non-detects were set to zero.

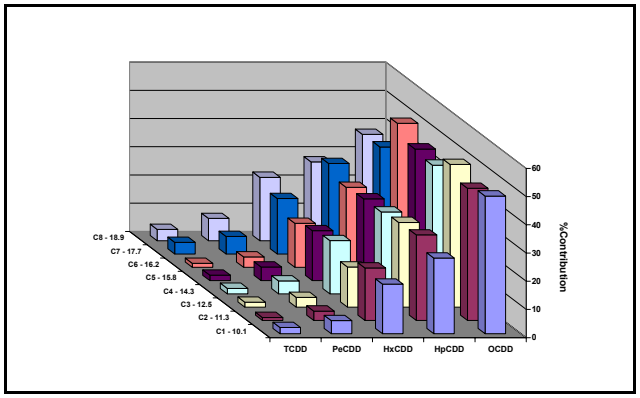

Figure 2. Tetra- to OCDD homologue contribution to the PCDDs along the depth of the core (meters BGS).

The toxic equivalents (TEQs) for the eight core samples range from 180 (C8) to 2,500 pg WHO-TEQ/g dm (C2). Mean and median concentrations are 980 and 930 pg WHO-TEQ/g dm, respectively. Figure 3 illustrates the percent contribution of each 2,3,7,8-substituted PCDD to the WHO-TEQs, and is presented in order of increasing PCDD contribution. It is apparent from Figure 3 that 1,2,3,7,8-PeCDD contributes most to the WHO-TEQ in each sample, with an average contribution of 41%. The second highest contributor is 1,2,3,7,8,9-HxCDD, contributing on average 24%. Although OCDD is found at the highest concentration throughout the core, it only contributes on average 0.3% to the WHO-TEQ.

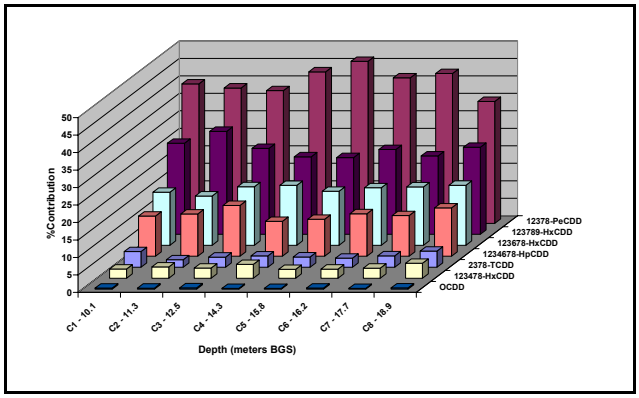

Figure 3. Percent 2,3,7,8-substituted PCDD contribution to the WHO-TEQs.

Discussion

The congener profiles, high PCDD concentrations, and low and undetectable levels of PCDFs in each sample of the core are similar to what others have observed in kaolin and ball clay samples [1, 2, 3]. However, one difference is the HeptaCDD ratio in the samples analyzed in this study. In this study, 1,2,3,4,6,7,8-HpCDD was on average 2.1 times greater than 1,2,3,4,6,7,9-HpCDD. The mean 1,2,3,4,6,7,8-HpCDD/,1,2,3,4,6,7,9-HpCDD ratio reported by Ferrario et al., was 0.67 [1]. Additionally, Prange *et al*., reported that 1,2,3,4,6,7,9-HpCDD was between 1.2 and 2.8 times greater than 1,2,3,4,6,7,8-HpCDD in kaolin samples from Queensland, Australia [4]. If dechlorination reactions are occurring within these environmental samples, the difference in the HeptaCDD ratios from different locations may indicate there is more than one physiochemical or biological process responsible.

Data from this study are the first to provide information on the vertical changes in both congener profile and concentrations within a clay core exhibiting the "natural formation" pattern. This PCDD/F data will be combined with the mineralogical analysis, currently being performed at the University of Notre Dame. This will allow the determination of the extent, if any, the mineralogy and, therefore, physiochemical processes play in the varying PCDD/F congener profiles and concentrations. With this information and data from two other clay cores from the same geological region, we expect to elucidate a plausible hypothesis as to the natural occurrence of dioxins in clay.

Acknowledgements

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