

## The Isomer Distribution and Congener Profile of Polychlorinated Dibenzo-p-dioxins (PCDDs) in Ball Clay from the Mississippi Embayment (Sledge, Mississippi)

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### Introduction

Several recent studies have found elevated levels of polychlorinated dibenzo-p-dioxins (PCDDs) in chickens<sup>1</sup> and farm raised catfish<sup>2</sup> grown in the United States resulting from the use of contaminated animal feed. The dioxins were discovered to have originated from the ball clay used as an anti-caking agent in the soybean meal component of the feed. This ball clay use as an animal feed additive has subsequently been discontinued. The ball clay was mined from an area geologically referred to as the Mississippi Embayment. However, the source and/or origin of the dioxins in this ball clay have yet to be discovered.

A useful method to help identify the source of an unknown complex chemical mixture like polychlorinated dibenzo-p-dioxins/-furans is to determine the distribution of the various congeners within a particular homolog group and to develop a profile of all the 2,3,7,8-chlorine substituted congeners. They can then be compared to the profiles and distributions of the PCDDs/PCDFs of known sources. Quite often the isomer distribution and congener profile is very characteristic of a particular source and is often referred to as a "chemical fingerprint". This information can be used as a means to help identify the origin of the material.

The congener profile and isomer distribution of PCDDs/PCDFs in the Mississippi ball clay has been established on a DB-5 analytical column and the chromatograms of the various congeners displayed using DB-5MS column.

### Methods & Materials

The ball clay samples were collected from the open pit mining facilities in Sledge, Mississippi. The PCDDs and PCDFs were extracted from the ball clay samples with benzene using a modified version of USEPA SW 846 Method 3540C (Soxhlet)<sup>3</sup>. The resulting extract was solvent exchanged to hexane and underwent column clean-up with acidified/basic silica gel, alumina, and PX-21 graphitized carbon<sup>4</sup>. Five gram samples were mixed with anhydrous sodium sulfate and fortified with <sup>13</sup>C recovery surrogates prior to extraction.

The samples were analyzed using both J&W Scientific DB-5, 60 meter x 0.32 mm (0.25  $\mu$ m film thickness) and DB5-MS, 60 meter x 0.32 mm (0.25  $\mu$ m film thickness) analytical capillary columns employing Hewlett Packard 5890 gas chromatographs. The

chromatographic conditions were as follows: injector temperature - 275 °C; interface temperature - 280 °C; initial temperature - 130 °C; initial hold time - 1 minute; rate 1 - 5 °C/min; hold time 15 minutes @ 235 °C; rate 2 - 6 °C/min; final temperature - 295 °C; column head pressure - 23 psi, carrier gas - helium. A Kratos Concept high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) operated on the lock mass drift correction mode was used for analysis.

Isomer identifications were initially established using a DB-5 column employing the use of authentic PCDDs standards (Cambridge Isotopes, Inc.), when available, and by the use of standard chromatographic techniques employing relative retention times (RRTs). Identifications not made using authentic standards were determined by generating RRTs and comparing them to those derived by Ryan *et al.*<sup>5</sup> under the chromatographic conditions described therein. The agreement of RRTs between laboratories was excellent. Isomer identifications were then made on the DB-5MS column using standards, by comparing the profile to those on the DB-5 and by the process of elimination.

## Results & Discussions

The isomer distribution of the tetra-, penta-, and hexa-chlorinated homologs are presented in Figure 1 and the congener profile and concentrations from two selected ball clay samples are presented in Figure 2. The hepta- and octa-chlorinated homologs profiles are unremarkable in that the heptas contain only two possible isomers and the octa only one and thus, the chromatograms are not displayed. The concentration of the 1,2,3,4,6,7,9-HpCDD is approximately 1.5 times greater than that of the 1,2,3,4,6,7,8-HpCDD and elutes first on both columns.

As is evident in Figure 1, the tetra profile is dominated by the 2,3,7,8-, 1,2,7,8-, 1,2,6,7-, and 1,2,8,9-congeners. This is in marked contrast to the profile exhibited by a "typical" air sample in which these isomers are minor components and the profiles are dominated by the 1,3,6,8-, 1,3,7,9-, 1,3,6,9-, and 1,2,4,9-/1,2,4,8 (unresolved) congener pair. Another interesting feature is the absence of any of the 2,3,7,8-Cl substituted furans at comparable concentrations to those found for the dioxins (Figure 2). The limit of detection (LOD) for these congeners is 0.4 parts per trillion (ppt). Another characteristic is that the 1,2,3,7,8,9-HxCDD is present at higher levels than the other 2,3,7,8-HxCDD isomers. This is unusual since, in most cases, the 1,2,3,6,7,8 is the dominant congener among the toxic hexa isomers, especially in biological media<sup>1,4,6,7</sup>. This situation regarding the hexa-isomers has also been observed by Rappe *et al.*<sup>8</sup> and seems to be a general trend for most food samples from around the world. However, this specific HxCDD distribution has been identified in Mississippi sediments without an anthropogenic input by Rappe *et al.*<sup>8</sup>. It is interesting to note that the tetra isomer distribution reported by Rappe *et al.* in catfish feed was dominated by the same congener pattern seen here and in chicken feed and both have been determined to have arisen from the use of ball clay in the soybean meal component of the feed. Moreover, the distinctive features of the 2,3,7,8-congener profile seen in the ball clay were also retained by the chicken and catfish. This demonstrates the conservative, stable, and reproducible nature of these isomer patterns and indicates their value as reliable indicators of their source and/or origin. However, there are instances when the congener profile is not indicative of

the original source<sup>10</sup>. Numerous congener profiles from the USEPA source inventory<sup>9</sup> have been examined and none of those examined share the characteristics of this ball clay. The source of the dioxins found in this ball clay has yet to be established. ECL is presently examining the known relationships between the various congeners present in specific profiles, their sources, and the processes and chemistry responsible for their occurrence.

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### References

1. Ferrario, J.; Byrne, C.; Lorber, M.; Saunders, P.; Leese, W.; Dupuy, A.; Winters, D.; Cleverly, D.; Schaum, J.; Pinky, P.; Deyrup, C.; Ellis, R.; Walcott, J. **1997**, *Organohalogen Compounds* 32: 245-251.
2. Cooper, K.; Bergek, S.; Fiedler, H.; Hjelt, M.; Bonner, M.; Howell, F.; Rappe, C. **1996**, *Organohalogen Compounds* 28: 197-202.
3. USEPA, **1998**, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW 846, Method 3560C, (Soxhlet), Washington, D.C., January, 1998.
4. Ferrario, J.; Byrne, C.; McDaniel, Dupuy, A. **1996**, *Anal. Chem.* 68(4): 647-652.
5. Ryan, J.; Conacher, H.; Panopio, L.; Lau, B.; Hardy, J.; Masuda, Y. **1991**, *Jour. Chromatog.* 541: 131-183.
6. Lorber, M.; Saunders, P.; Ferrario, J.; Leese, W.; Winters, D.; Cleverly, D.; Schaum, J.; Deyrup, C.; Ellis, R.; Walcott, J.; Dupuy, A.; Byrne, C.; McDaniel, D. **1997**, *Organohalogen Compounds* 32: 238-244.
7. Lorber, M.; Winters, D.; Griggs, J.; Cook, R.; Baker, S.; Byrne, C.; Dupuy, A.; Schaum, J. **1998**, *Organohalogen Compounds* 38: 125-129.
8. Rappe, C.; Bergek, S.; Fiedler, H.; Cooper, K. **1998**, *Chemosphere* 36(13): 2705-2720.
9. Cleverly, D.; Schaum, J.; Schweer, G.; Becker, J.; Winters, D. **1997**, *Organohalogen Compounds* 32: 430-435.
10. Lorber, M.; Pinsky, P.; Gehring, P.; Braverman, C.; Winters, D.; Sovocool, W. **1998** *Chemosphere* 37: 2173-2197.

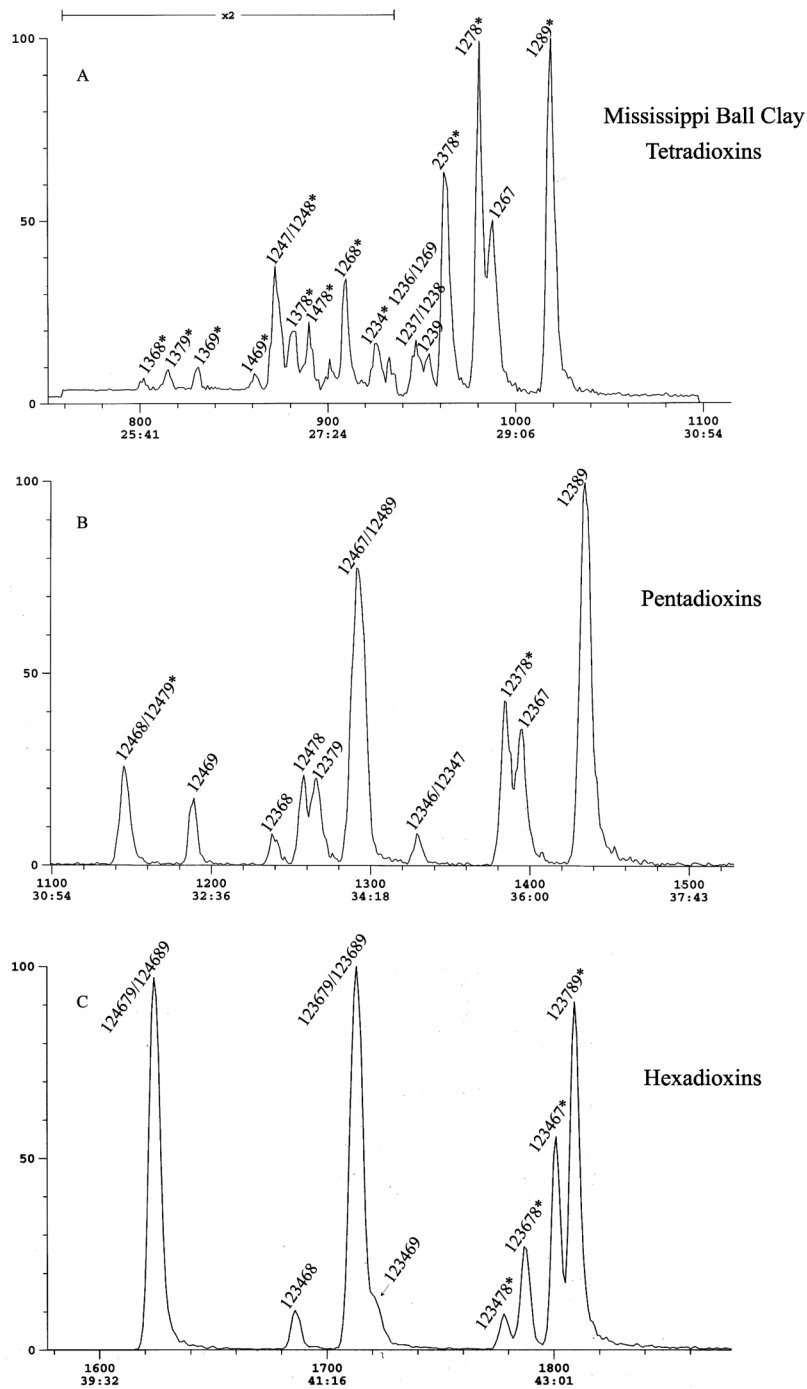


Figure 1. Isomer distribution of the tetra (A), penta (B), and hexa-chlorinated dioxins (C) in ball clay from Sledge, Mississippi. \*Verified using authentic analytical STD.

**Congener Profile & Concentration of PCDDs/PCDFs in Ball Clay**

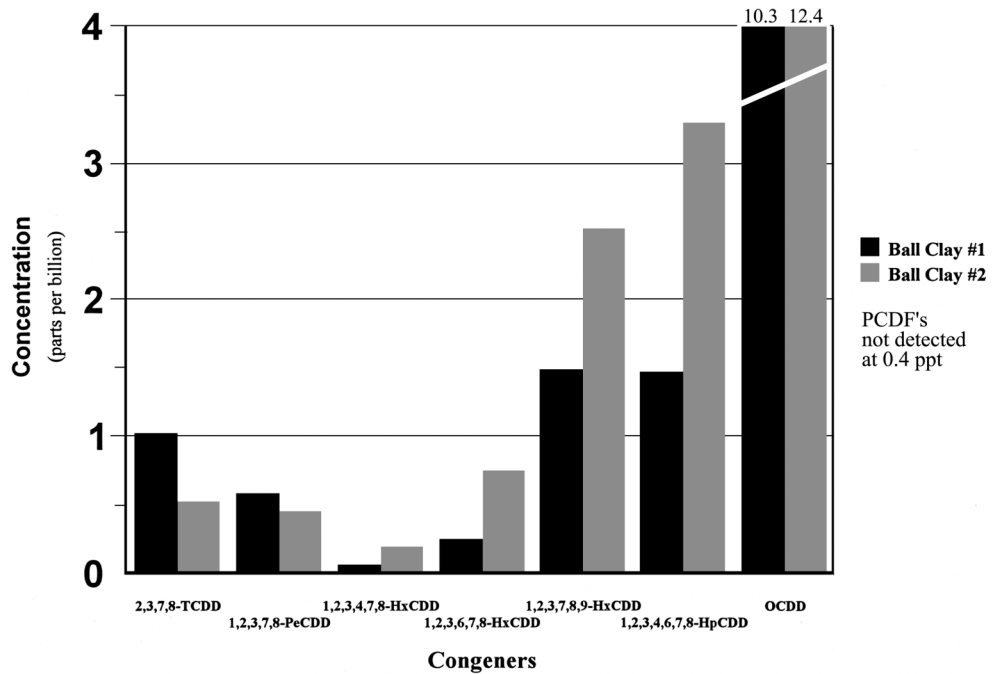


Figure 2.