# THE POSSIBLE ROLE OF OXIDES AND/OR ELEMENTS IN THE TRANSFORMATION OF PCDDs IN US BALL CLAY EXHIBITING
# THE 'NATURAL FORMATION' PATTERN

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**Introduction**

At Dioxin 2003, we reported the 2,3,7,8-substituted PCDD/F results from the analysis of a ball clay core exhibiting the "natural formation" pattern from Kentucky, USA.[1] In general, all 8 samples contained elevated levels of 2,3,7,8-PCDDs, with increasing PCDD concentrations with increasing chlorine substitution. Moreover, furans were only detected in two of the samples at extremely low concentrations. WHO-TEQs ranged from 180 to 2,500 pg WHO-TEQ/g dm, with 1,2,3,7,8-PeCDD and 1,2,3,7,8,9-HxCDD contributing most to the TEQ. The results from that study were the first to provide information on the vertical changes in both PCDD congener profile and concentrations within a clay core exhibiting this unique "natural formation" pattern. In addition, it confirmed the pattern found by others in ball clay and kaolin samples from different regions of the United States, Germany, and Spain.[2, 3, 4, 5]

Although all samples from that study exhibit the "natural formation" pattern, one noticeable difference was the heptaCDD ratio. 1,2,3,4,6,7,8-HpCDD was on average 2.1 times greater than 1,2,3,4,6,7,9-HpCDD. This is in direct contrast to what others have reported for ball clay, kaolin, and even sediment samples displaying this unique PCDD/F congener profile.[2, 6, 7] Ferrario *et al*., reported a mean 1,2,3,4,6,7,8-HpCDD/1,2,3,4,6,7,9-HpCDD ratio of 0.67.[2] Prange *et al.,* found that this ratio ranged from 0.36 to 0.83 in kaolin samples from Queensland, Australia.[7]

In this study, we report isomer specific PCDD results from the analysis of the ball clay core samples from Kentucky to determine if the dechlorination pattern observed is similar to what Gaus *et al*. found.[6] Also, Principal Component Analysis (PCA) was used to evaluate the isomer specific data along with the bulk mineralogical, elemental and oxide analyses. The possible role of oxides and/or elements aiding in the dechlorination is discussed.

**Methods and Materials**

*PCDD/F Analysis*

The PCDD/F analysis is described elsewhere.[1] The 2,3,7,8-substituted PCDD results from that study were used to determine congener specific concentrations.[1] Separation was performed on a 60 m JW DB-5 column.

*Bulk Mineralogy*

X-ray diffraction (XRD) was performed on each corresponding duplicate sample stored at the University of Notre Dame, USA using a Rigaku Miniflex Diffractometer with CuKα 1.540562 wavelength radiation and a nickel monochromator. The samples were run from 3° to 80° 2θ with a step size of 0.02 and a count time of 0.6 seconds. Each sample was run four times; bulk, air-dried, ethylene glycolated, and heat treated to 300°C.  On completion of the X-ray diffraction, Jade© version 3.1 software was used to identify the mineral assemblages.

*Elemental Analysis*

The elemental and oxide values reported in this study were determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) or Inductively Coupled Plasma Quadrapool Mass Spectrometry (ICP-QMS).  All analyses were performed by Analytica in Luleå, Sweden.

**Results and Discussion**

*Isomer Specific Results*

Using isomer specific data, Gaus *et al*., observed a unique dechlorination pattern throughout the depth of two sediment cores from Queensland, Australia.[6]  The authors proposed that the transformation processes (anaerobic dechlorination in particular) produced a PCDD profile that resulted in a distinct dominance of congeners chlorinated in the 1,4,6,9-positions.  The 1,2,3,4,6,7,9-HpCDD/1,2,3,4,6,7,8-HpCDD ratio was found to increase with depth and hence had a direct correlation to an increase in lower chlorinated 1,4,6,9-congeners.

Because the initial 2,3,7,8-substituted PCDD results we reported at Dioxin 2003 exhibited a contrasting heptaCDD ratio from what others have reported, we performed isomer specific evaluation of the data.  Figure 1 illustrates the isomer specific distribution of tetra to hepta PCDDs from the eight strata analyzed from the ball clay core.  Figure 1 shows that there is neither a substantial change in contribution with depth nor a dominance of the "1,4,6,9-pattern" throughout this core.  The average contribution of the 1,4,6,9-substituted isomers from the various homologue groups throughout the core was: 34% among the HpCDDs, 22% among all 10 HxCDDs, 11% among all 14 PeCDDs, and 37% among all 22 TCDDs.  Gaus *et al.,* by comparison, reported average 1,4,6,9-substituted isomer contributions for two sediment cores of, 80% and 84% among the HpCDDs, 77% and 87% among the HxCDDs, 34% and 53% among the PeCDDs, and 25% and 57% among the TCDDs.[6]
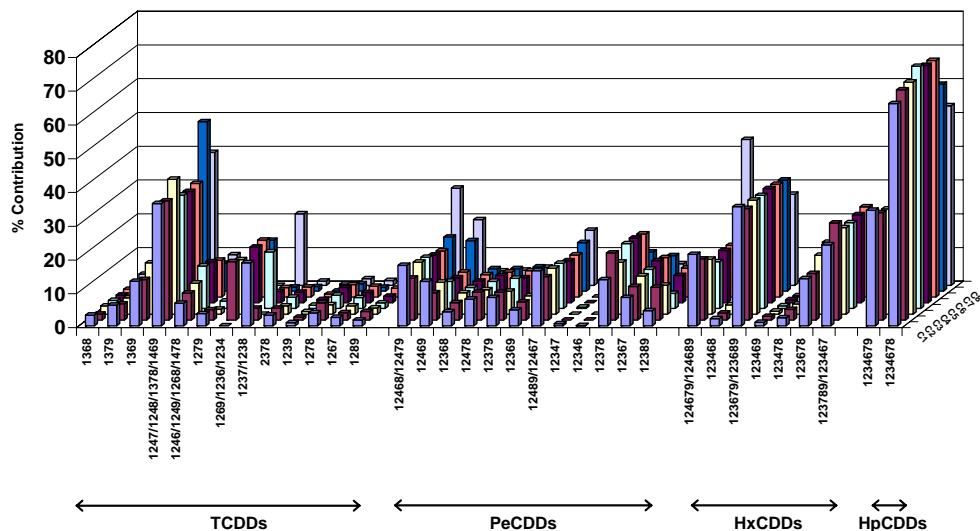
**Figure 1.** Isomer specific contribution of tetra to heptachlorinated PCDDs throughout the length of the ball clay core.

Figure 2 shows the PCA score and loading plots of the 1,4,6,9-congener and homologue contribution data. The two-component model presented explained 91.4% (74.2% and 17.2%, respectively) of the variance in the data set. As can be seen in the score plot, samples C-1, C-2, C-4 and C-5 are clustered together to the left side of Figure 2a. The corresponding loading plot (Figure 2b.) shows that these four samples contain a relatively higher degree of %OCDD as compared to samples C-7 and C-8. The later two samples are characterized by a higher degree of %HxCDD and %TCDD. The second dimension, separating C-7 and C-8 is dominated by %HpCDD.

The isomer specific results from this ball clay core demonstrates that the 1,4,6,9-pattern is not always dominant in environmental matrices exhibiting the natural formation pattern. Further, these data suggest that there are more than one physiochemical or biological processes responsible for the observed dechlorination patterns observed among different ball clay and sediment cores.[6, 8]

*Ball Clay Characterization*
In 2001, Rappe *et al*., reported the chemical composition of four US ball clay, three US kaolin and four German kaolin samples.[4] The chemical composition data indicated similar elemental composition in the US ball clay and German kaolin. Interestingly, the US kaolin samples, which had the lowest PCDD concentrations, deviated from the US ball clay and German kaolin with respect to elemental composition. With the knowledge from that previous study, we determined the bulk mineralogy and elemental composition of the samples from this clay core study. This was

done to determine if the concentrations or specific elements and/or oxides can be correlated with the unique PCDD congener profile we observe throughout the clay core.
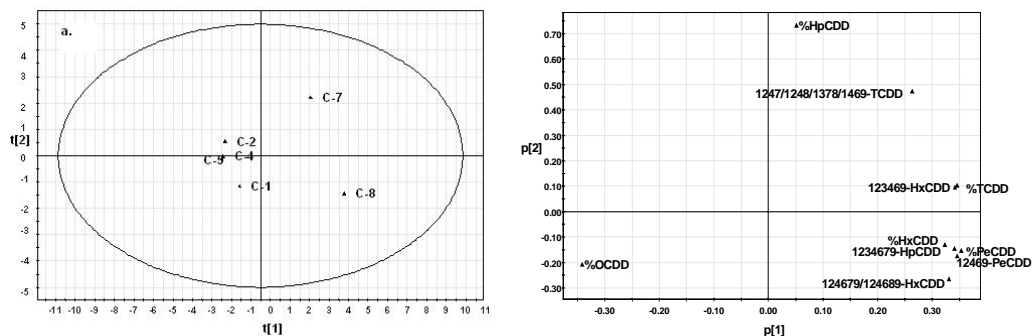


**Figure 2.** (a) The score and (b) corresponding loading plot based on 1,4,6,9-isomer and homologue contribution data for Core C.

Table 1 includes the data from the bulk mineralogical analyses. The dominant mineral throughout the core is smectite, with an average value of 33%. Kaolinite, chlorite, illite and quartz are also present at mean values of 23, 20, 17, and 8%, respectively. Overall, there is no substantial variation in bulk mineralogy of the strata throughout the core.

**Table 1:** Bulk mineralogy results from XRD analysis throughout the length of the ball clay core.

| Sample | Depth (meters BGS) | %Kaolinite | %Illite | %Smectite | %Quartz | %Chlorite |
|--------|--------------------|------------|---------|-----------|---------|-----------|
| C-1 | 10.1 | 20 | 20 | 35 | 5 | 20 |
| C-2 | 11.3 | 20 | 15 | 35 | 5 | 25 |
| C-3 | 12.5 | 25 | 15 | 30 | 5 | 25 |
| C-4 | 14.3 | 30 | 15 | 35 | 5 | 15 |
| C-5 | 15.8 | 25 | 15 | 25 | 10 | 25 |
| C-6 | 16.2 | 15 | 20 | 30 | 10 | 25 |
| C-7 | 17.7 | 20 | 20 | 35 | 10 | 15 |
| C-8 | 18.9 | 25 | 15 | 40 | 10 | 10 |

Table 2 presents data from the elemental and oxide analyses of 6 samples from Core C. The oxides are shown as the percentage of total solids (TS), whereas the elemental data is expressed as mg/kg TS. $SiO_2$ and $Al_2O_3$ are the dominant oxides throughout the core. Elements found in the highest concentrations are Ba, Cr, Sr, V, Zn, and Zr.

Figure 3 shows the PCA score and loading plots of the bulk mineralogy, oxide, and elemental data. There does not seem to be a correlation between the elemental and oxide data with the PCDD homologue and/or 1,4,6,9-pattern contributions throughout this core. Therefore, the data in Figure

3 do not contain homologue or 1,4,6,9-pattern contributions. The two-component model presented explained 77.3% of the variance in the data set. PC one (t1), explained 49.6% of the variance, which is dominated by an array of oxides and elements to the left (e.g., MgO, Sr, CaO, and V) and $TiO_2$, and smectite towards the right of the loading plot. The second PC (t2) explained 27.7% of the variance, which is dominated by e.g., MnO and Be.

Although there is not a definitive indication from these data that specific elements and/or oxides are aiding in the dechlorination, there are similarities between certain strata throughout the core with respect to the bulk mineralogy, oxide and elemental data. C-1 and C-2 form the first cluster, C-4 and C-5 the second, and C-7 and C-8 the third. Although we reported (at Dioxin 2003) that there was no clear trend of PCDD concentrations with depth, samples C-7 and C-8 have considerably lower PCDD concentrations than the other samples in the core. This supports the hypothesis that the abundance of certain oxides and/or elements may be responsible for the lower PCDD concentrations and different dechlorination pattern towards the bottom of the core. Further research is needed to support this theory.

*Continuing Work*
Results from this study are being used to interpret PCDD data from two other ball clay cores from the United States.[8] Elemental and oxide analyses were determined for the samples reported for the two additional cores. Because a broad range of PCDD concentrations were observed within the same core and among the three clay cores, it should be possible to determine with greater certainty what role, if any, particular oxides and/or elements play in the dechlorination process.

**Table 2:** Elemental and oxide analysis results.  Note that two of the samples, C-3 and C-6 were not sent for analysis and thus are not reported herein.

| ELEMENT | SAMPLE | C-1 | C-2 | C-4 | C-5 | C-7 | C-8 |
|---|---|---|---|---|---|---|---|
| **Total Solids (TS)** | % | 95.5 | 96 | 95.1 | 95.2 | 96.4 | 96.6 |
| **SiO2** | % TS | 57.7 | 60.3 | 56.1 | 56.2 | 62.2 | 65.8 |
| **Al2O3** | % TS | 21.4 | 20.5 | 21.8 | 22.1 | 18.3 | 16.4 |
| **CaO** | % TS | 0.51 | 0.47 | 0.55 | 0.55 | 0.46 | 0.44 |
| **Fe2O3** | % TS | 4.28 | 4.76 | 6.55 | 6.24 | 5.73 | 5.37 |
| **K2O** | % TS | 1.68 | 1.62 | 1.67 | 1.64 | 1.72 | 1.79 |
| **MgO** | % TS | 1.28 | 1.18 | 1.41 | 1.39 | 1.23 | 1.17 |
| **MnO** | % TS | 0.027 | 0.041 | 0.059 | 0.059 | 0.069 | 0.063 |
| **Na2O** | % TS | 0.152 | 0.135 | 0.124 | 0.113 | 0.127 | 0.143 |
| **P2O5** | % TS | 0.061 | 0.062 | 0.079 | 0.078 | 0.074 | 0.073 |
| **TiO2** | % TS | 0.966 | 1.090 | 0.894 | 0.905 | 0.996 | 1.000 |
| **Ba** | mg/kg TS | 358 | 335 | 382 | 381 | 404 | 551 |
| **Be** | mg/kg TS | 7.33 | 4.65 | 2.76 | 2.9 | 2.45 | 2.07 |
| **Co** | mg/kg TS | 24.1 | 23.3 | 14.4 | 18.4 | 23.8 | 22.4 |
| **Cr** | mg/kg TS | 109 | 117 | 107 | 107 | 121 | 121 |
| **Cu** | mg/kg TS | 27.4 | 29.9 | 54.8 | 34.4 | 30.8 | 21.1 |
| **La** | mg/kg TS | 53.7 | 44.8 | 44.4 | 50.9 | 49.9 | 42.4 |
| **Nb** | mg/kg TS | 21.8 | 23.3 | 21.3 | 22 | 23.8 | 22.9 |
| **Ni** | mg/kg TS | 45.4 | 53.7 | 34.7 | 36.1 | 38.2 | 48.8 |
| **Sc** | mg/kg TS | 16.5 | 16.2 | 17.2 | 17.4 | 15.1 | 13.7 |
| **Sr** | mg/kg TS | 112 | 107 | 118 | 122 | 107 | 104 |
| **V** | mg/kg TS | 150 | 143 | 161 | 163 | 135 | 122 |
| **Y** | mg/kg TS | 38 | 33.2 | 27.1 | 27.2 | 29.8 | 29.8 |
| **Zn** | mg/kg TS | 145 | 158 | 105 | 402 | 145 | 84.5 |
| **Zr** | mg/kg TS | 219 | 244 | 186 | 196 | 282 | 298 |
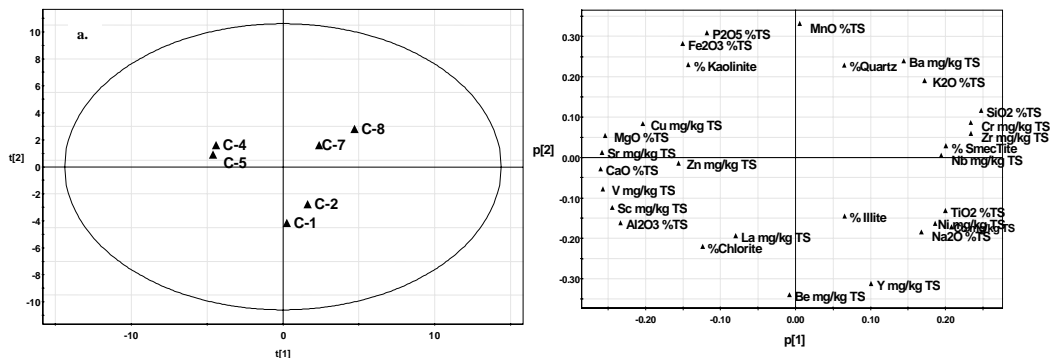
**Figure 3.** (a) The score and (b) corresponding loading plot based on bulk mineralogy, oxide and elemental data for Core C.

## Acknowledgement

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