Characterization of Organic Matter in US Ball Clay Exhibiting the 'Natural Formation' Profile utilizing Pyrolysis-GC/MS: Trends between PCDD Homologue Distributions and Specific Pyrolysis Products

Damien Gadomski[1], Dan White[2], Robert Irvine[1], Mats Tysklind[3]

[1]University of Notre Dame, Notre Dame
[2]University of Alaska Fairbanks, Fairbanks
[3]Umeå University, Umeå

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, Germany, and Spain [1, 2, 3, 4, 5]. 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 homologue. 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. To date, the natural processes that produce and/or transform the PCDDs observed in these clay samples are not known.

Recently, we reported the PCDD and bulk mineralogical results of an extensive ball clay study from three cores located in three different geological areas in the United States [6]. All samples contained elevated levels of PCDDs, with low and mostly undetectable levels of PCDFs. The maximum toxic equivalents (TEQs) for the three cores were 2,500, 440, and 15,000 pg WHO-TEQ/g dw, respectively. This study was the first to compare and contrast the vertical distribution of PCDD concentrations and isomer-specific contributions throughout ball clay cores exhibiting the 'natural formation' pattern. There was no apparent correlation between PCDD concentrations and/or homologue profiles with the bulk mineralogy or organic carbon (OC). However, this study demonstrated that there are remarkably different PCDD homologue profiles both among the cores and within them [6].

In the present study, we report 2,3,7,8-substituted PCDD and pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) results from the analyses of five US ball clay samples. The correlations between specific pyrolysis products and the varying PCDD homologue contributions among the five samples are discussed.

Methods and Materials

PCDD/F Analysis

Each sample was homogenized before extraction. Sixteen 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).

Pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS) Analysis

Each duplicate sample was sent to the University of Alaska, Fairbanks for py-GC/MS analysis. A sample of dried ball clay containing approximately 150 µg C was pyrolyzed in a quartz sample tube. Pyrolysis was performed on a CDS Analytical Pyroprobe 2000/AS2500. The pyrolyzer was connected to an HP 6890 gas chromatograph (GC) in tandem with an HP 5973 mass selective detector (MSD) operated in electron impact (EI) mode. Compounds were separated in the GC using a Restek Rtx35-MS column (30m x 0.32mm x 0.25µm). The pyrolysis interface temperature was held constant at 280ºC. The pyrolysis reaction chamber was programmed to ramp at 10ºC/msec from the interface temperature to 700ºC and hold at 700ºC for 10 seconds. The GC was run for 1 minute with pulsed splitless injection at 25 psi with a temperature program of 40ºC for 30 min, ramp at 1ºC /min to 120ºC, ramp at 2ºC/min to 220ºC, and a final ramp at 10ºC/min to 280ºC and hold for 10 minutes to clean the column before the next run. The program was run with a constant 2.0 ml/min flow of helium gas. Mass spectra were identified using the Wiley 275 library. Clean sample tubes were run every fourth sample to prevent and/or detect any carry-over.

An index of 30 compounds were selected from each chromatogram, identified, and grouped into 9 classes based on the probable origin of each compound. The areas of all 30 index compounds in each chromatogram were summed to find the total index area for each chromatogram. For every sample, the “fraction of index” for each of the nine compound classes was calculated by summing the areas of all compounds in each class and dividing by the total index area.

Results and Discussion

PCDD Results

Results from the 2,3,7,8-substituted PCDD/F analyses are shown in Table 1. Sample ‘A’ is from a different core than the other four samples. The differences in both PCDD concentration and WHO-TEQ values for samples ‘C1’ and ‘C2,’ are significant. The black carbonaceous matter was separated from ‘C1’ (by visual separation with forceps) and combined with ‘C2’ before homogenization. The LOI only increased by 24% between samples ‘C1’ and ‘C2’ (presumably due to the simple separation technique involved), yet the ∑PCDDs and TEQ increased by 2.4 and 3.3 times, respectively in ‘C2.’ This clearly demonstrates the importance of characterizing the carbonaceous impurities usually associated with ball clay in order to better understand the possible origin of the PCDDs found in this matrix.

Py-GC/MS Results

The percent contribution of seven of the nine compound classes for each sample from the py-GC/MS analyses are shown in Figure 1. Two of the compound classes (primary and secondary polysaccharides) were below the limit of detection for all five clay samples. It is clear from Figure 1 that sample 'A' and 'D' are quite similar being dominated by naphthalenes at 100 and 90.3%, respectively. These two samples have the highest contribution of OCDD to the ∑PCDDs and the lowest WHO-TEQs. Interestingly, these two samples come from two separate ball clay cores, approximately 160 km apart (and different relative elevations within the two cores; 'A' was sampled at the top, whereas 'D' was sampled 15.2 meters below the top of the other core).

Table 1: 2,3,7,8-substituted PCDD data for the five samples analyzed. All concentrations are in pg/g dw. The only PCDF above the limit of detection was OCDF in sample 'A' at 6.4 pg/g dw.

Sample ID	A	B	C1	C2	D
LOI	2.23%	9.87%	1.82%	2.26%	0.90%
2,3,7,8-TCDD	22	1100	61	140	41
SUM TCDDs	110	42000	1200	3600	860
%Total of PCDDs	0.03	7.18	1.15	1.43	0.09
1,2,3,7,8-PeCDD	84	7900	555	1800	240
SUM PeCDDs	630	73000	3650	11000	3300
%Total of PCDDs	0.20	12.48	3.50	4.37	0.33
1,2,3,4,7,8-HxCDD	190	4000	440	1500	370
1,2,3,6,7,8-HxCDD	160	6600	695	2100	360
1,2,3,7,8,9-HxCDD	460	42000	3000	11000	1800
SUM HxCDDs	2800	160000	13500	46000	13000
%Total of PCDDs	0.87	27.35	12.96	18.28	1.32
1,2,3,4,6,7,8-HpCDD	3200	80000	10400	31000	16000
Sum HpCDDs	7700	180000	27000	81000	40000
% of Total PCDDs	2.40	30.77	25.97	32.19	4.05
OCDD	310000	130000	58500	110000	930000
%total PCDD	96.50	22.22	56.42	43.72	94.21
Sum PCDDs	321240	585000	103850	251600	987160
pg WHO-TEQ/g dw	250	15073	1139	3721	787

Additional evaluation of these data showed a direct correlation ($r^2 = 0.8896$) between the percent contribution of OCDD to the ∑PCDDs and the amount of naphthalenes among the five samples (Figure 2a). Furthermore, there is an inverse correlation ($r^2 = 0.9621$) between the percent contribution of HpCDDs to the ∑PCDDs and the amount of naphthalene (Figure 2b). These are pyrolysis data therefore the naphthalene found in these ball clay samples was not naphthalene itself, but a pyrolysis product of a larger molecule. Aromatic structures in pyrolysis are generally derived from aging lignin fragments [7].

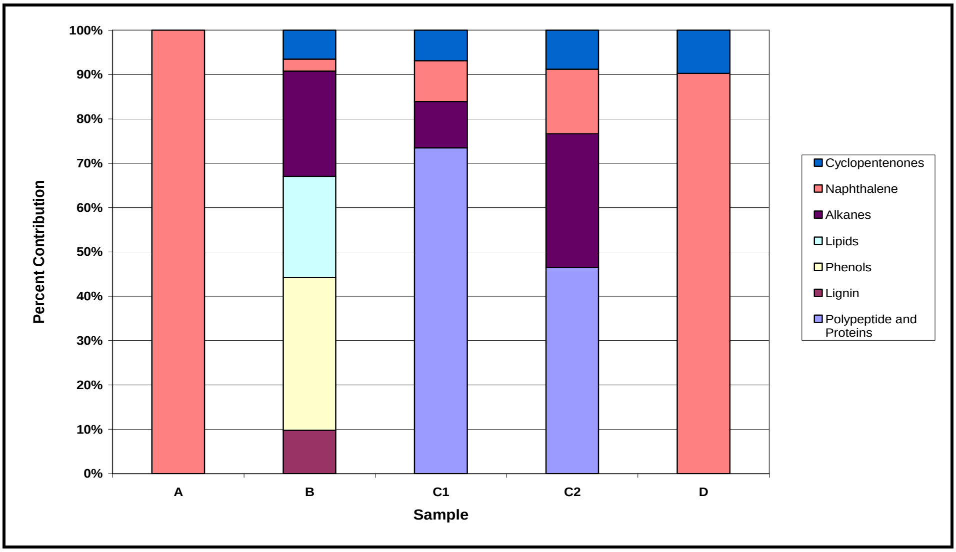

Figure 1. Py-GC/MS data for the five ball clay samples, shown as percent contribution for seven of the nine compound classes. Primary and secondary polysaccharides were below the limit of detection for all five clay samples.

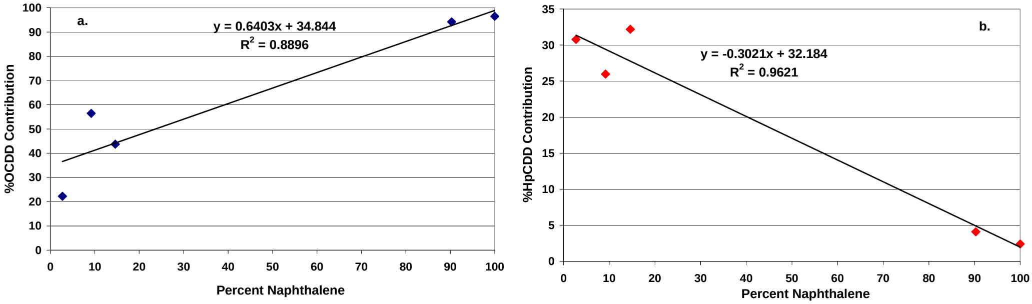

Figure 2. (a) Illustrates the direct correlation of the percent contribution of OCDD to the ∑PCDDs versus percent naphthalene. (b) Illustrates the inverse correlation of the percent contribution of HpCDD to the ∑PCDDs versus percent naphthalene.

Figure 3 shows the Principal Component Analysis (PCA) score (a) and corresponding loading plot (b) used to evaluate the PCDD homologue contribution data along with the specific alkane, cyclopentenone, and naphthalene compounds. The two-component model presented explained 91.7% (67.5 and 24.2%, respectively) of the variance in the data set. Lipids, phenol and lignin compounds were only associated with sample 'B,' and polypeptides and proteins only with 'C1' and 'C2,' therefore this data was not included in the model. There was no apparent correlation between 2,3,7,8-substituted PCDD concentrations and the py-GC/MS data; therefore, it was also excluded from the model.

Not surprisingly, samples ‘A’ and ‘D’ are clustered together towards the right of the score plot (Figure 3a) due to their high contribution of naphthalene and %OCDD. Sample ‘B’ falls to the lower left of the score plot due to its higher contribution of lower chlorinated congeners but it is also the only sample to contain decane (8.57%) as a pyrolysis product. The separation of samples ‘C1’ and ‘C2’ is due to the higher concentration of alkanes in sample ‘C2,’ especially hexadecane, tridecane, and pentadecane.

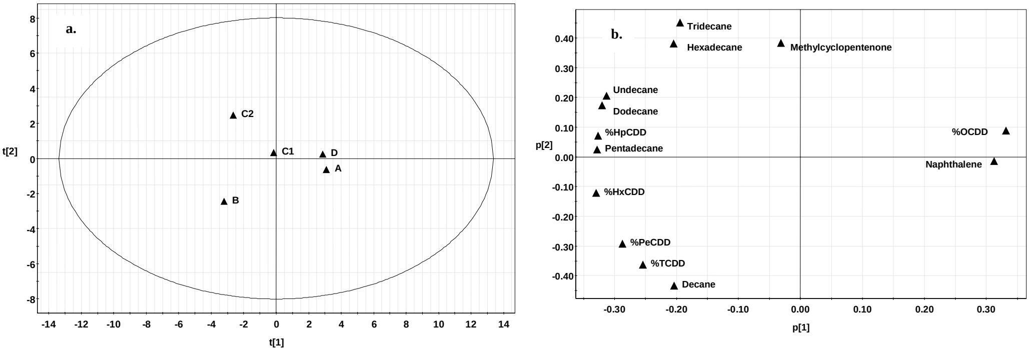

Figure 3. The PCA Score (a) and corresponding Loading Plot (b) based on PCDD homologue contribution, percent naphthalene contribution, as well as specific alkane and cyclopentenone contributions.

Continuing Work

The results from this study indicate that there are correlations between the abundance of specific organic matter pyrolysis products and the contrasting PCDD homologue profiles found in the different ball clay samples. This preliminary set of data suggests that the characterization of the organic matter found in ball clay may be a key step to developing a plausible formation and/or transformation hypothesis for the occurrence of PCDDs found in this matrix. Therefore, the data from additional py-GC/MS analyses of ball clay, kaolin, and sediment samples exhibiting the ‘natural formation’ pattern will be interpreted with the corresponding PCDD/F data to help aid in that goal.

Acknowledgement

This research was sponsored by Georgia-Pacific Corporation, Atlanta, Georgia, USA and the United States Department of Education. We would also like to thank Sarah Seelen for running the Pyrolysis-GC samples.

References

1. Gadomski, D., Tysklind, M., Irvine, R.L., Burns, P.C., Andersson, R., and Talalas, T. (2003) Organohalogen Compounds 61, 373.
2. Ferrario, J.B., Byrne, C.J. and Cleverly, D.H. (2000) Environ. Science and Technol. 34, 4524.
3. Ferrario, J.B., McDaniel, D. and Byrne, C. (1999) Organohalogen Compounds 40, 95.
4. Rappe, C., Tysklind, M., Andersson, R., Burns, P.C. and Irvine, R.L. (2001) Organohalogen Compounds 51, 259.
5. Abad, E., Llerena, J.J., Sauló, J., Caixach, J., Rivera, J. (2002) Chemosphere 46, 1417.
6. Gadomski, D., Tysklind, M., Irvine, R.L., Burns, P.C., Andersson, R. (2004) Environ. Sci. and Technol. (Submitted).
7. Bracewell, J. et al (1989) Humic Substances II: In Search of Structure, M. H. B. Hayes et al, eds,. John Wiley and Sons, New York, pp.181-222.