

SOUR I

Formation of PCDDs and PCDFs in high yields in the reactions of chlorophenols over fly ash

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Abstract. High yields of PCDDs were formed when chlorinated phenols were passed over incinerator ash at 250 - 350°C. Only a few congeners were formed which differentiates this reaction from the typical *de novo* reaction first observed by Stieglitz-Vogg which yields a multitude of congeners. An ash from an incinerator burning chlorophenol waste gave up to 10% conversion to PCDDs, an ash from an MSW incinerator gave more than 40% conversion.

Key words. Chlorophenols, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, formation, ash catalyzed, 280-350°C.

INTRODUCTION

In 1991 it was reported that cow's milk from three farms in the Bolsover area in Derbyshire, England had elevated concentrations of 2,3,7,8-tetra CDD as well as other 2,3,7,8-substituted PCDDs (1,2). Subsequent analyses of soil and herbage samples from the area indicated a specific "Bolsover pattern" dominated by two early eluting non-2,3,7,8-substituted tetra- CDDs, three early eluting non-2,3,7,8-substituted penta CDDs and one non-2,3,7,8-substituted tetra CDF (3).

A chemical plant producing chlorophenols is situated in the area. Residues, primarily distillation bottoms, were incinerated, and the incinerator was suggested to be the source of the contamination(3). PCDDs and PCDFs were also found in the feedstock (3), but a careful comparison between the feedstock and the "Bolsover pattern" showed that the majority of the PCDDs and PCDFs were in fact formed during the incineration process (4). The incinerator was normally operating well above 800°C. A system of hot oil tubes was placed in the back-side of the oven, locally reducing the temperature of the flue gas.

Two different mechanisms are discussed for the formation of PCDDs and PCDFs during incineration

- a) Formation in the furnace
- b) Formation during the cooling phase.

It is now generally accepted that in most cases the formation during the cooling phase dominates. This *de novo* reaction is catalyzed by copper or copper salts, (5). It is also known that these reactions result in a multitude of different PCDDs and PCDFs (6)

(the "incineration pattern"), which is quite different from the pattern found in samples from the Bolsover area.

In 1987 Karasek and Dickson (7) and Dickson and Karasek (8) reported that a series of PCDDs could be formed in a fly ash catalyzed reaction from chlorophenols at 250-350°C.

In 1993 Altwicker and Milligan investigated the conversion of 2,3,4,6-tetrachlorophenol to PCDDs on fly ash and found this reaction to be 100 times faster under laboratory conditions than a *de novo* reaction using non-extractable carbon (9). The same authors found the formation depended on the ash used, the concentration of chlorophenol in the gas phase, reaction time and reaction temperature (10).

The purpose of the laboratory studies reported here was an analysis of quantities, congener profiles and congener patterns produced from the reaction of selected chlorophenols using the Bolsover ash for comparison to an ash from a normal municipal solid waste (MSW) incinerator.

EXPERIMENTAL

Two ash samples were used in this study. One was collected in the Bolsover on the hot oil coils incinerator and the other is a fly ash from an MSW incinerator from the American continent.

The experiments were performed in a fixed-bed reactor as described in Reference 10. The reaction time was 5 minutes, the gas flow 80 mL/min. Amounts of ash, chlorophenols and reaction temperatures are reported in Table 1. The ash samples were cleaned by Soxhlet extraction for 50 hours using toluene. The cleaned ash was re-extracted once more showing only minor amounts of PCDDs were present after the first Soxhlet extraction. The ash cleaned once was used for the experiments. The extracts were cleaned and analyzed by HRGC/HRMS using a 60 m Supelco SP-2330 column and a VG 70 E mass spectrometer operating at a resolution of 5 000, see also Marklund (11).

RESULTS

Conversion rate

The results obtained in this study are collected in Table 1.

For the experiments with 2,3,4,6-tetrachlorophenol performed at 299°C the yield for the Bolsover ash was slightly higher than for the MSW fly ash. Increasing the temperature for the Bolsover ash to 323°C decreased the conversion rate drastically (CA 20).

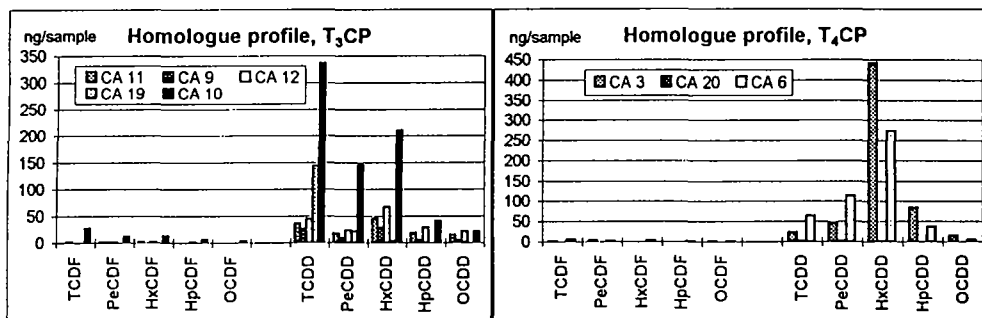


Figure 1.

Figure 2.

Table 1. Condition and yields of the experiments

Sample name	Sample description	Temp (°C)	Total PCDD/F (ng/sample)	Yield (%)
CA 3	0.50 g Bolsover ash + 13 000 ng T ₄ CP	299	619	4.8
CA 6	0.50 g MSW fly ash + 13 000 ng T ₄ CP	299	511	3.9
CA 9	0.48 g Bolsover ash + 2 000 ng T ₃ CP	299	78.0	3.9
CA 10	0.50 g MSW fly ash + 2 000 ng T ₃ CP	299	818	41
CA 11	0.48 g Bolsover ash + 2 000 ng T ₃ CP	277	139	6.9
CA 12	0.48 g Bolsover ash + 2 000 ng T ₃ CP	323	189	9.5
CA 19	0.50 g Bolsover ash + 2 000 ng T ₃ CP	353	171	8.6
CA 20	0.50 g Bolsover ash + 13 000 ng T ₄ CP	323	6.16	<0.1

For the experiments with 2,4,6-trichlorophenol at 299°C, the MSW fly ash was much more efficient, the yield in this experiment was as high as 41%. For the Bolsover ash higher conversion rates were observed for lower as well as higher temperatures, the highest yield was observed at 323°C (9.5%).

Homologue profiles

The homologue profiles are given in Figure 1 and 2. In addition to the "dimerization" products, both ashes resulted in products with additional chlorine substitution as well as dechlorination. Experiments with 2,4,6-trichlorophenol gave both hepta- and octa-CDD.

A difference was found between the two ashes. The MSW fly ash gave more PCDFs than the Bolsover ash.

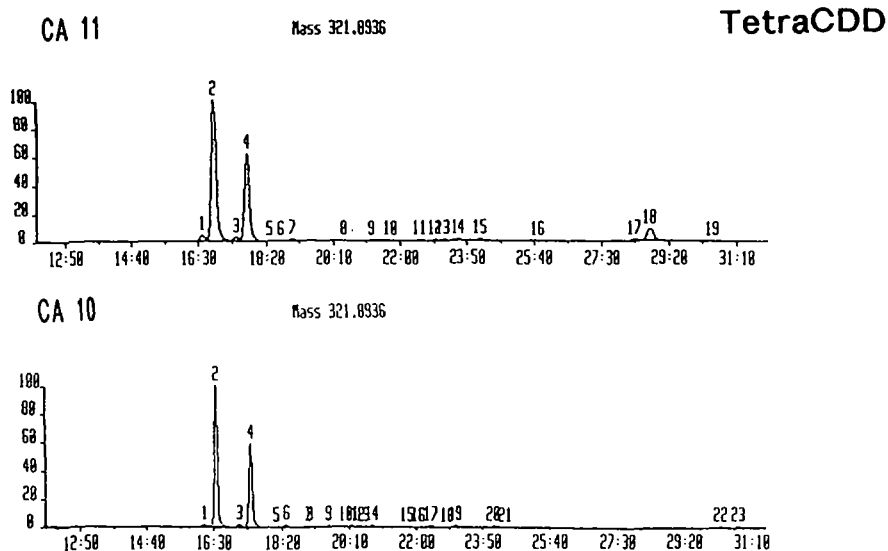


Figure 3.

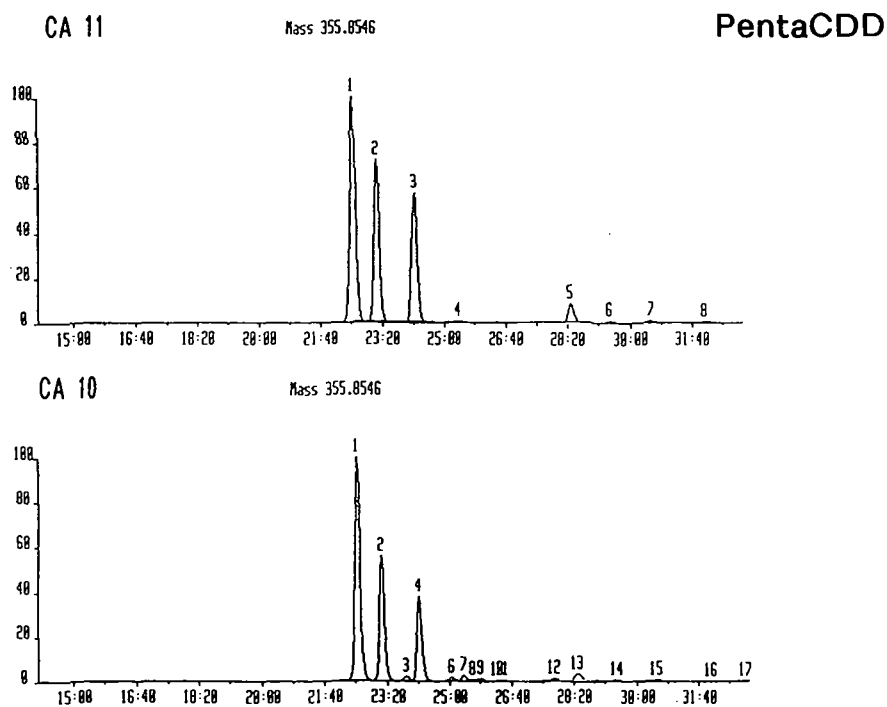


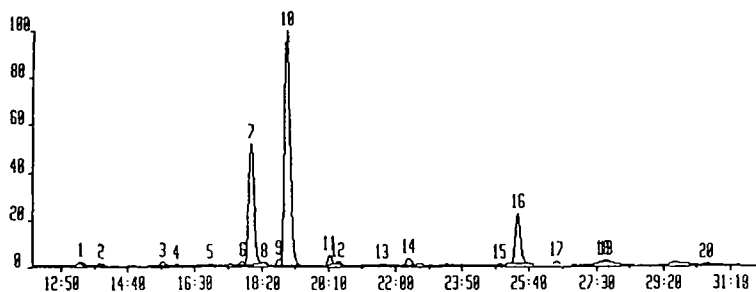
Figure 4.

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CA 11

Mass 385.8587

TetraCDF



CA 10

Mass 385.8587

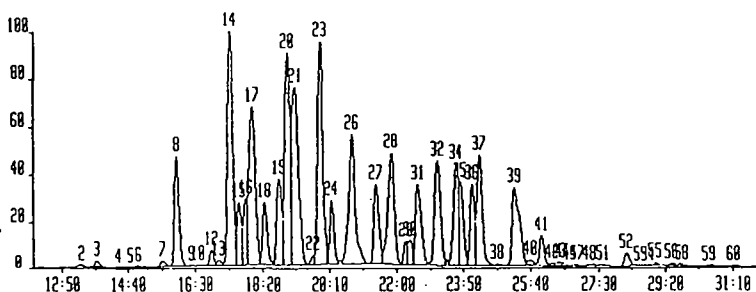
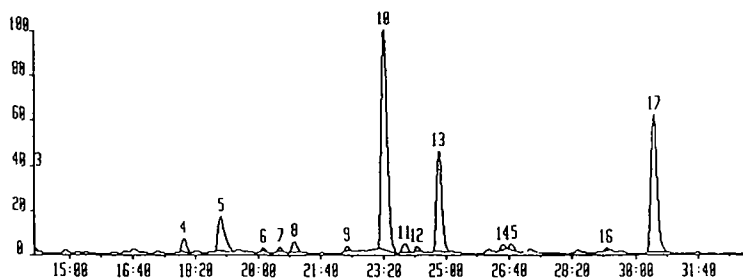


Figure 5.

CA 11

Mass 339.8597

PentaCDF



CA 10

Mass 339.8597

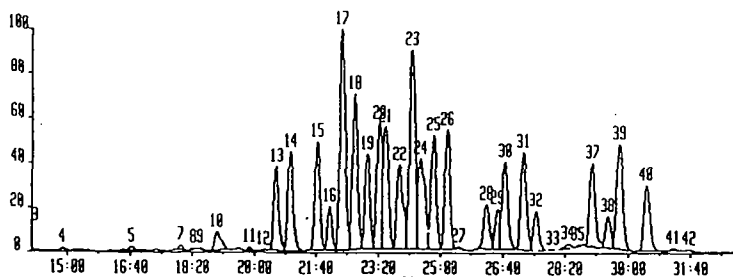


Figure 6.

Homologue group pattern

The homologue group pattern for the PCDDs are almost identical for the two ashes, illustrated in Figure 3, for the tetra CDDs and Figure 4 for the penta CDDs. For the experiments with 2,4,6-trichlorophenol and the Bolsover ash and MSW. This pattern contains the isomers indicated; this is identical to the typical "Bolsover" pattern.

However, for the PCDFs, the situation is quite different, see Figures 5 and 6. For the MSW fly ash a multitude of peaks were formed resulting in the normal "incineration pattern" (6). The Bolsover ash gave only one tetra CDF peak, the 1,2,3,7-/1,4,7,8-tetra CDF. This peak is the dominating peak of the PCDFs in the "Bolsover pattern" (Figure 5).

CONCLUSIONS

Conversions to PCDD/F up to 40% can be obtained by passing chlorophenols over ash at temperatures around 300°C.

Only a few PCDD congeners are formed but some are the result of either dechlorination and chlorination reactions. An MSW fly ash gave the typical "incineration pattern" for the PCDFs, while the Bolsover ash yielded only a few congeners (Cl₄ - Cl₆).

The typical products formed from the Bolsover ash agree with the pattern found in the Bolsover region showing that the major part of the dioxins emitted from the incinerator was produced by the ash catalyzed formation of PCDDs and PCDFs in the condensation reactions of chlorophenols. This formation takes place on the hot oil coils, where the temperature is optimal for this formation.

REFERENCES

1. Food Safety Directorate News Release, FSD 64/91, October 1991.
2. Dioxins in Food. Food Surveillance Paper No. 31. Ministry of Agriculture, Fisheries and Food. London: HMSO, 1992.
3. Holmes, S.J., Jones, K.C. and Miller, C.E. Organohalogen Compounds, **24**, 373.
4. Rappe, C. Expert Report. Case No.T 950208. The Crown Court at Leicester, UK.
5. Vogg, H. and Stieglitz, L. Chemosphere, **15**, 1373 (1986).
6. Rappe, C. Fresenius' J. Anal. Chem., **348**, 63 (1994).
7. Karasek, F.W. and Dickson, L.C. Science, **237**, 754 (1987).
8. Dickson, L.C. and Karasek, F.W. J. Chromatogr., **389**, 127.
9. Altwicker, E., Milligan, M.S. Chemosphere, **27**, 301 (1993).
10. Milligan, M.S. and Altwicker, E.R. Environ. Sci. Technol., **30**, 225 (1996).
11. Marklund, S. Emissions and Environmental Emissions. Thesis, Umeå University, 1990.