

## TEMPERATURE AND CONCENTRATION EFFECTS ON THE DIOXIN AND FURAN FORMATION FROM A MIXTURE OF CHLOROPHENOLS OVER FLY ASH

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### Introduction

Monitoring polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) emissions from combustion processes through direct measurements of surrogate compounds<sup>1-6</sup>, such as chlorophenols, would bring the opportunity to control and limit the formation of PCDD/F from municipal waste incinerators (MWIs). Chlorophenols (CPs) have been studied as precursors to PCDD/F formation but generally these experiments have been carried out with unrepresentative concentrations and potentially overlapping formation mechanisms. Weber and Hagenmaier<sup>7</sup> reported the temperature dependence of the combustion products from chlorophenols in the gas phase. Milligan and Altwicker<sup>8</sup> demonstrated that the kinetics of PCDD formation from chlorophenol over fly ash is strongly dependent on the chlorophenol precursor concentration. The present contribution is focused on combustion conditions characteristic of MWI flue gases, such as very low levels (ppb concentrations) of precursors and the presence of water vapor. Further, an oxidized fly ash (carbon free, to avoid *de novo* contribution) is used. By changing reaction conditions of temperature and gas phase precursor concentration, this work attempts to establish the relationship between specific CP reactants and the resultant PCDD/F congener products.

### Materials and Methods

Four chlorophenols (CPs) typically found in municipal waste incinerator (MWI) flue gas were used as reactants: 2-chlorophenol (2CP), 2,4-dichlorophenol (24DCP), 2,4,6-trichlorophenol (246T3CP), and 2,3,4,6-tetrachlorophenol (2346T4CP). The experimental set-up is illustrated in Figure 1. A system consisting of capillary tubes and reservoirs contained in a temperature-programmable oven<sup>9</sup>, delivered a constant, low concentration of input CPs. The CP vapor mixtures were conveyed in a total flow of 4.5 L/min of nitrogen (N<sub>2</sub>) containing 10% oxygen (O<sub>2</sub>) and 1% water (H<sub>2</sub>O) vapor. This gas stream of reactants was transported through heated transfer lines to a pre-combustion mixing chamber before entering two isothermally heated reactors set in parallel. Each reactor consisted of a tubular fixed bed of 33 cm in length and 2.1 cm internal diameter, with a coarse ground glass frit in the tube center to support the fly ash bed contained between two glass wool plugs. The beds were composed of 0.5 g of carbon free (oxidized) fly ash (U.S. EPA OX FA)<sup>10</sup> (90 µm) mechanically mixed with 4.5 g of glass beads to facilitate the flow. A clean tube reactor and fresh bed were used for each run. The experiments were performed over 4 h by sampling a slip stream (2 L/min) of the total vapor mixture through each bed; the remaining flow (0.5 L/min) exited through an atmospheric exhaust to prevent system over pressure that may affect the injection rate of the CPs. Moreover, to control the consistency of the experiments, all of the flow was sampled before and after each run through three dichloromethane- (DCM, methylene chloride) filled impingers, which were then concentrated together and analyzed to verify the CP input concentrations. After each bed, the exhaust gas was sampled using a modified EPA Method 23 XAD trap pre-spiked with a mixture containing isotopically-labeled analogs of some of the target compounds for data quality determination. The target compounds were mono- to octa- PCDDs/Fs and mono- to penta- CPs. Analysis of the reaction bed fraction revealed that less than 1% of the products (as un-reacted chlorophenols and PCDD/F) were found in the solid phase. The analysis was then focused only on the gas phase sample in the XAD trap fraction. For each experiment, the XAD trap was analyzed after being spiked with internal standards (additional isotopically-labeled analogs of the target compounds). These samples were Soxhlet extracted for 16-24 h with methylene chloride. For PCDD/F quantification, half of the sample was cleaned up and analyzed by High Resolution

## Thermal processes

Gas Chromatography/ Low Resolution Mass Spectrometry (HRGC/LRMS) with a J&W DB-Dioxin capillary column of length 60 m, i.d. 0.25 mm, and phase 0.15  $\mu\text{m}$  film according to the modified EPA Method 23. The detection limit was about 2.5 ng/peak for all PCDDs/Fs. Quantifications of semi-volatile target compounds other than PCDD/Fs were measured in the other half of the sample using a HRGC/LRMS with a J&W DB-5 capillary column of length 60 m, i.d. 0.25 mm, and phase 0.25  $\mu\text{m}$ . Each experiment has been replicate three or four times.

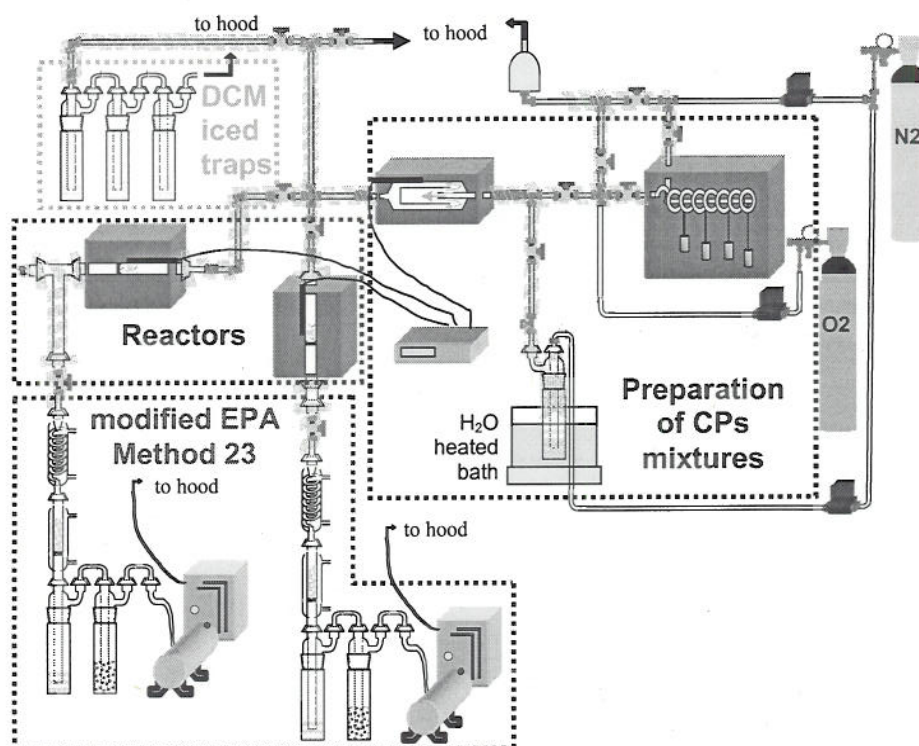


Figure 1- Experimental set-up

### Results and discussion

To examine the effect of temperature on the formation of PCDDs/Fs, experiments were conducted at temperatures ranging from 280 °C to 420 °C in 30-40 °C increments. Based on the vapor pressure of the compounds, the parameters of the delivery system (temperature, tube lengths) were chosen to obtain 48 ppb of 2CP, 28 ppb of 24DCP, 100 ppb of 246T3CP, and 60 ppb of 2346T4CP. The yields of each PCDD and PCDF homologue and the yields of the homologue sum (totPCDDs and totPCDFs) are shown in Figure 2 as a function of the reactor temperature (yields are expressed as percent conversion of phenol, meaning chlorophenols). The total conversion of chlorophenols was calculated by subtracting the un-reacted fraction of total CPs measured in the gas phase from the total input quantity of CPs passing through the bed.

As found in previous studies on condensation of CPs over model fly ash<sup>11-14</sup>, PCDD formation dominated PCDF formation. In the temperature range studied, all the different homologues were produced except for the mono-CDD which was found only in infinitesimal quantity at 310 and 345 °C and the hepta- and octa-CDD which were not produced at 280 °C. The most abundant PCDD homologues were the tetra-, tri- and penta-CDDs for temperatures between 280-345 °C; at 385 °C and 420 °C the di-CDD started to dominate the homologue pattern. At 385 °C the di-CDD levels are higher than the tri-CDD but still lower than the tetra-CDD until at 420 °C where it is the major PCDD homologue formed. The highest PCDD yields were produced around 310 °C in our experimental conditions.



From studies with 2346T4CP at 150 ng/mL (17 ppm), Milligan and Altwicker<sup>8</sup> reported a maximum PCDD yield around 350 °C, but at higher gas phase precursor concentration no maxima were observed. Regarding the PCDFs results in this current work, mono- and di-CDF were the highest homologues formed (except at 280 °C where only trace quantities of hexa- and hepta-CDF were generated). Contrary to that observed for the PCDD homologue profiles, the temperature change seemed to have minimal effect on the quantity of PCDF formed.

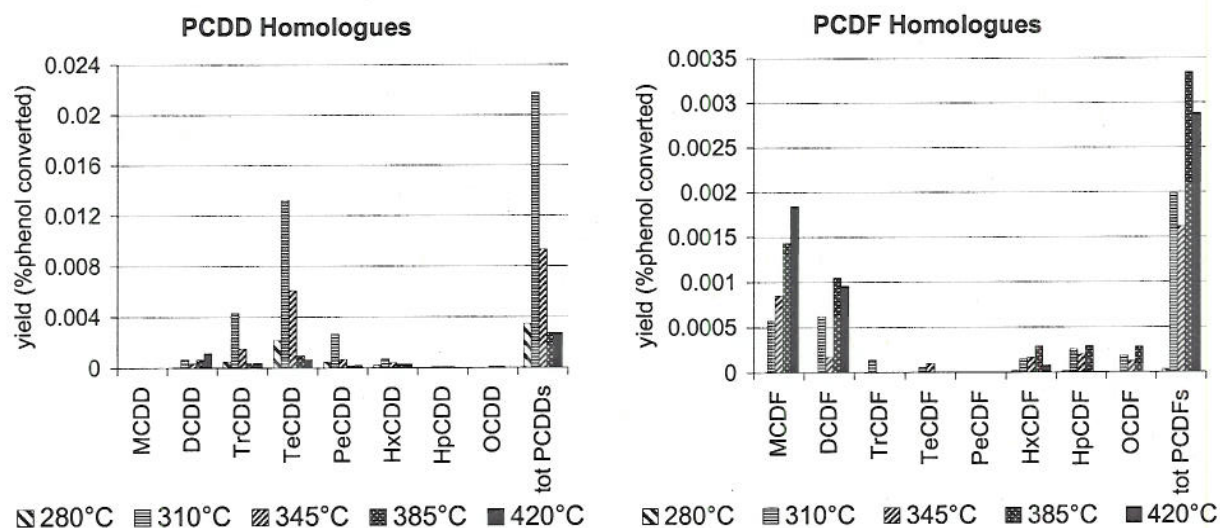


Figure 2 - Effect of temperature on PCDDs/Fs formation

To analyze the impact of the input CP concentration on the formation of PCDDs, a set of three experiments of different CP mixtures was conducted at 310 °C: (i) the 2CP was around 1-2 ppb, the 24DCP around 2-4 ppb, the 246T3CP around 4-6 ppb, and the 2346T4CP around 1-2 ppb, (ii) the input CPs concentrations in the second set were 20 times higher than (i), (iii) the concentrations were 45 times higher than (i). Figures 3a and 3b show respectively, the quantity (in nanomoles) and the yields of PCDD homologues generated from the three mixtures. Similar trends were observed in all the experiments conducted at this temperature. As expected<sup>8</sup>, the quantity of PCDDs produced increased with increasing input CPs concentration. However, the yields of PCDDs were ten times higher when the input concentrations were lower. Subsequent experiments performed at double the reactant concentration [(ii) and (iii)] had little impact on the PCDD yields. As this set of experiments [(ii) and (iii)] had only been performed at one temperature, we could suspect that the maximum PCDD formation was not yet reached for experiments with higher gas-phase precursor concentration. Nevertheless, the input CP concentrations of the (ii) experiment are almost the same as those used to examine the effect of temperature (reported previously in this paper). Therefore, it seems that chlorophenols lose their ability to convert into PCDD over fly ash when increasing their gas phase concentration. Regarding the PCDFs, increasing the concentrations of the reactants did not increase the concentration of the homologues already formed but did yield more homologues; thus increased the quantity of total PCDFs. Concerning the yields of PCDFs, similar trend to PCDDs yields was observed. The precursor concentrations typically found in the flue gas of municipal waste incinerators are well known to be from 1 to 10  $\mu\text{g}/\text{Nm}^3$ . This condition was satisfied with the (i) experiments, while the other experiments (ii and iii) have been performed at much higher level. Cieplik et al.<sup>15</sup> points out recently that at realistic levels (ppb) the "precursor" pathway appears to become of comparable importance to the *de novo* pathway, and that the PCDF:PCDD ratios of these two contributions are close to those observed in MWI.

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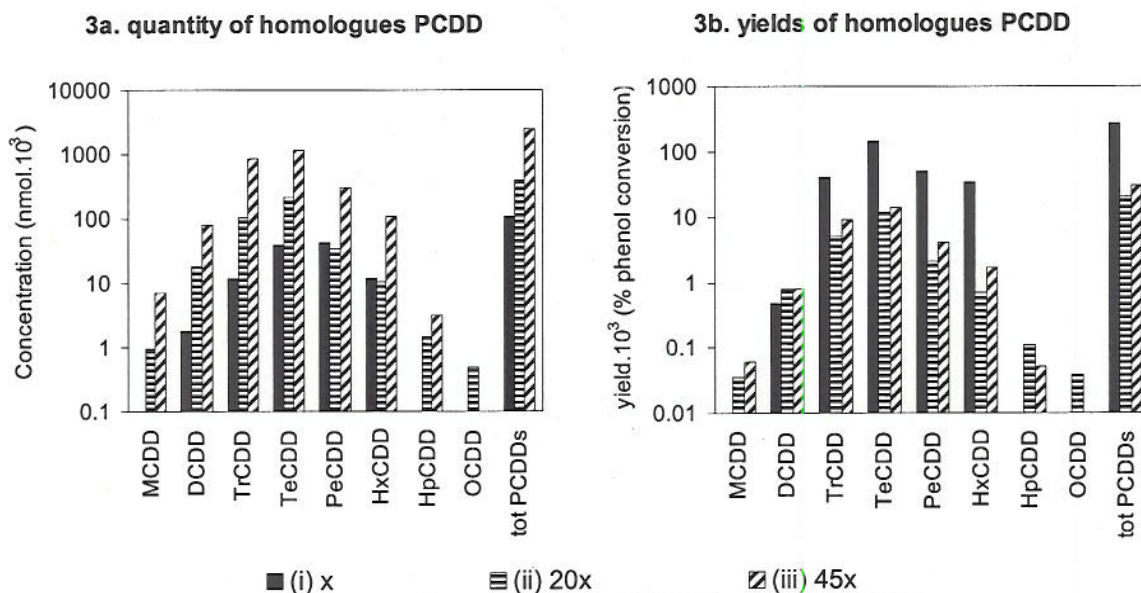


Figure 3- Impact of concentration on PCDD formation at 310 °C

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