

Dioxin and Furan Formation on Fly Ash from Mixture of Chlorophenols

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Introduction

There is a growing tendency to monitor polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) emissions from combustion processes through direct measurements of surrogate target compounds¹⁻⁸ most likely to be formed through pathways that are parallel (or have related mechanisms) or involved in PCDD/F formation.

The aim of this study is to draw correlations between the emission profile distribution of the PCDDs/Fs and specific chlorophenol (CP) congeners that are typically found in combustion gas. The measurement of specific chlorophenol compounds in combustion gas (typically at ppb concentrations), with techniques such as jet resonance-enhanced multiphoton ionization/time-of flight mass spectrometry (jet REMPI/TOFMS), may be used as indirect measurements of PCDDs/Fs (typically at ppq concentrations)^{2,3,9}.

To establish the relationship between specific CP congener distributions and the PCDD/F products, this work investigated the formation of PCDDs/Fs from different CP mixtures passed over fly ash under selected reaction conditions (e.g., temperature and flue gas composition). This work attempts to relate incinerator measurements (e.g., realistic CP concentrations) and laboratory studies on PCDD/F formation (product distribution, yields, and rates) from CPs. Unlike prior extensive research in this area¹⁰⁻¹⁴, this work focused on concentrations (low ppb) and CP mixture ratios that are characteristic of raw municipal waste incinerator flue gas.

Materials and Methods

The experimental set-up consists of a diffusion delivery system, a pre-combustion mixing chamber, and an isothermally heated reactor as illustrated in Figure 1. Vapor mixtures containing different inputs of one to four CP at ppb concentrations were used: 2-3 ppb of 2-chlorophenol (2CP), 5-6 ppb of 2,4-dichlorophenol (24DCP), 9-12 ppb of 2,4,6-trichlorophenol (246T3CP), and 4-7 ppb of 2,3,4,6-tetrachlorophenol (2346T4CP). The CP vapor mixtures were conveyed in a total flow of 5 L/min of nitrogen (N₂) containing 10% oxygen (O₂) and 5% water (H₂O) vapor.

Experiments were conducted in a tubular fixed bed flow reactor, 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. The bed was composed of 0.5 g of carbon free (oxidized) fly ash (U.S. EPA OX FA)¹⁵ (150 mesh) mechanically mixed with 4.5 g of glass beads to facilitate the flow. The delivery system consisted of a capillary tube diffusion system contained within a temperature-programmable oven¹⁶. The experiments were performed at 310 °C for 4 h by sampling a slip stream (2 L/min) of the total vapor mixture through the bed to avoid any pressure build-up in the reactor system that may affect the injection rate of the CPs. Reference conditions were run to examine the reactivity of CPs in an empty reactor tube and through a bed of pure glass beads. Any CP residual in the lines of the delivery system was removed by passing nitrogen at 300 °C overnight. The gas exiting the reactor bed 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. For each experiment, the XAD trap and reaction bed fractions were analyzed separately 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 both fractions, followed by a 16-24 h Soxhlet extraction with toluene for the fly ash bed fraction. For PCDD/F quantification, half of the sample was cleaned up and analyzed by High Resolution Gas Chromatography/ Low Resolution Mass Spectrometry (HRGC/LRMS) with a J&W DB-Dioxin column 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 column.

Before and after each experiment, the input concentrations were verified by passing all of the flow upstream of the reaction furnace through three methylene chloride filled impingers which were then concentrated together and analyzed for CPs.

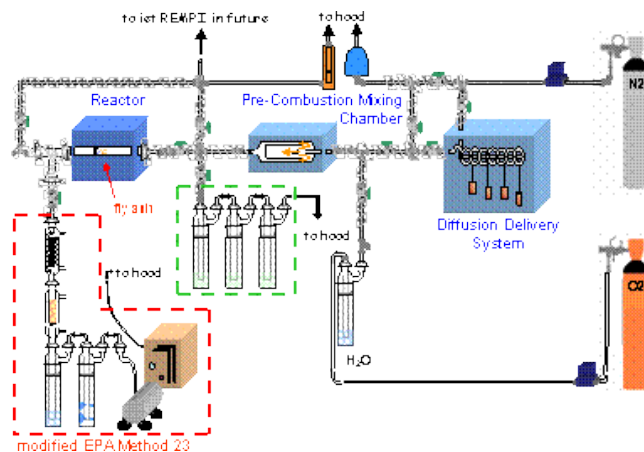


Figure 1- Experimental set-up

Results and discussion

To examine the effect of specific chlorophenols on the formation of PCDDs/Fs, a set of four experiments of different CP mixtures was conducted: (i) all four CPs included as discussed above, (ii) 24DCP + 246T3CP + 2346T4CP, (iii) 24DCP + 2346T4CP and (iv) 24DCP. The total quantities of the PCDD/F homologues formed in each of the four experiments are shown in Figure 2. As found in previous studies on condensation of CPs over model fly ash¹¹⁻¹⁴, PCDD formation dominated PCDF formation with all four experimental mixtures. The most abundant homologues formed were Tri-, Tetra-, Penta- and Hexa-CDDs. In experiment (ii), only the less-chlorinated PCDD congeners (DCDD, TriCDD) were affected by the removal of 2CP. With mixture (iii), the removal of both 2CP and 246T3CP resulted in an overall reduction in the Tetra- thru Hexa-CDD congeners. The decrease in the Tri- thru Penta-CDDs is consistent with the mechanism by which the most important isomers are formed via direct reactions involving 246T3CP (such as 1,3,6,8- and 1,3,7,9-TetraCDD). For the HexaCDD isomers, which can be theoretically expected from reaction between two molecules of 2346T4CP, some intermediate reactions must have been eliminated since removal of 2CP and 246T3CP resulted in a significant decrease of HexaCDD. The amounts of PCDFs formed were too close to the detection limit to allow for any conclusions to be deduced.

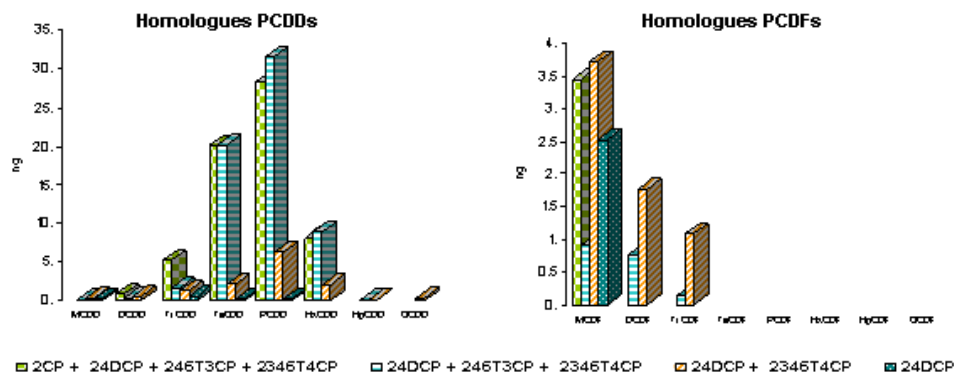


Figure 2- The Effect of the CP Input Mixture on (a)PCDD and (b)PCDF Formation

To investigate the impact of water vapor present during realistic combustion conditions on the heterogeneous formation of PCDD/F from CPs, an experiment with the original four CP input mixture was conducted in the absence

of water in the gas stream. The PCDD and PCDF yields compared to those using the same mixture with water in the gas stream are shown in Figure 3. The absence of water enhanced formation of all PCDD and PCDF homologues (except OCDD and OCDF). This effect was more significant for PCDDs, without affecting the homologue pattern. On the contrary, the removal of water resulted in the formation of more PCDF homologues than observed in the presence of water vapor. The lower effect on PCDFs may be due to the fact that the CPs used here are mostly involved in PCDD production rather than that of PCDF^{11,12,14}. Our results are apparently in contradiction to the experiments of Stieglitz et al.¹⁷ which report an increase in the yield of PCDD from oxidized fly ash (mixed with active charcoal) at 300 °C when water vapor was added in the gas stream. However, at the same temperature with charcoal/MgSiO₂/CuCl₂ in air, Jay et al.¹⁸ also reported a decrease in the total amount of PCDDs/Fs formed in presence of water. One of the possible effects of water could be to create additional oxygen or OH radical sources affecting catalyst surface reactions, both of which have an important role in PCDD and PCDF formation reactions.

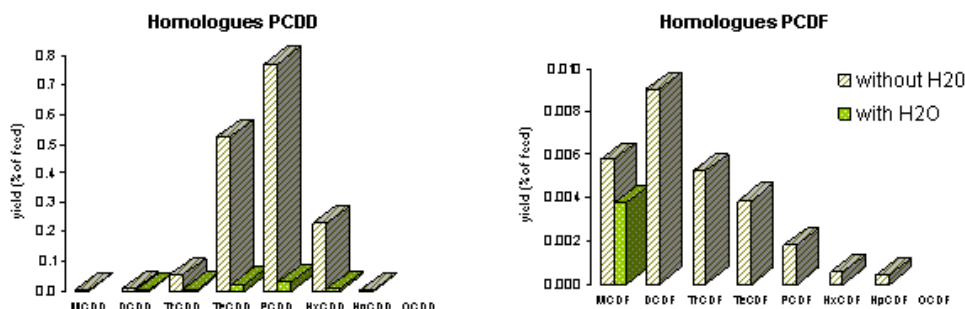


Figure 3- impact of water on PCDD/F formation

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