Proving of a hypothesis of thermal PCDF formation in laboratory scale furnace

Marchela Pandelova[1], Dieter Lenoir[1], Karl-Werner Schramm[1]

[1]GSF-Research Center for Environment and Health

Introduction

The correlation between PCDD/F and PCB in emissions is not so widely investigated as other indicator parameters such as PCBz and PCPh. Theroutine measurements of PCDD/Fs and PCBs are difficult and expensive. As a consequence, there is a growing tendency to find surrogates of PCDD/Fs. In particular chlorobenzenes have attracted much attention because of their good correlation with PCDD/F I-TEQ [1, 2, 3]. On the other hand the correlation between the PCB and PCDD/F is important in order to understand the mechanisms of PCDD/F formation. As a result of many investigations, the precursor combustion [4] and de novo combustion [5] has been developed to describe the formation pathway of PCDD/F in the stack gas of incinerators. Both mechanisms show the role of PCB molecules in PCDD/F formation [6].

The present study focus on the formation pathway of TCDF and PeCDF in order to prove the hypothesis of PCDF precursor theory. The correlation between the tetra- and pentachlorinated PCDF, PCB and PCBz values inthe flue gas of co-combustion of solid waste and coal in a laboratory scale furnace is used as a proof.Furthermore the influence of different inhibitors on these linear regressions is also studied.

Materials and Methods

A mixture of lignite coal, solid waste and PVC was thermally treated in a laboratory-scale furnace at 400°C [7]. Three different additives named $(NH_4)_2SO_4$, $(NH_4)_2S_2O_3$ and $(NH_2)_2CO$+S (1:1) used at level of 10% could suppress the PCDD/F, PCB and PCBz emission by more than 95-99%. Therefore, further experiments were performed in which these substances constituted a lower fraction of the fuel. Experiments wherein $(NH_4)_2SO_4$ and $(NH_4)_2S_2O_3$ were studied at 5 %, 3 % and 1 % of the total fuel weight were performed in triplicate and $(NH_2)_2CO$+S (1:1) studied at 3 % and 1 % of the total fuel weight was also examined. One sample of 5% $(NH_4)_2S_2O_3$ added to the fuel was excluded in this serial of investigations. Totally 21 samples including one sample treated without inhibitor and twenty other samples treated with different percentage of inhibitors was used in this investigation.

Once the experiment of thermal treatment was completed, the sample was processed by further specific clean-up steps. Quantification of PCDD/F, PCB and PCBz was performed on a high-resolution gas chromatograph coupled with a high-resolution mass spectrometer (HRGC/HRMS). The tetra- to octachloro- PCDD and PCDF, the tetra- to hepta- PCB and the tetra- to hexaPCBz congeners were identified and quantified in pg / g combusted material[8, 9]. In this work the concentrations of 2,3,7,8-TCDF; 2,3,4,7,8-PeCDF; PCB#153; PCB#180; 1,2,4,5-TCBz and PeCBzwere studied in order to find a linear regression between and prove the hypothesis of precursors theory of PCDF formation. The correlation between these compounds was studied independently for the samples with higher and lower toxicity.

Results and Discussion

It was found that with decreasing percentage of inhibitor the effect of PCDD/F formation is correspondently reduced [7]. The samples with lower concentrations of the investigated toxic compounds or samples treated with higher percentage such as 5% and 3% of the inhibitor were belonging to the samples with lower toxicity. The remaining samples form the group of the higher toxicity samples. Based on the precursor theory formation of TCDF and PeCDF compounds (Fig. 1) the correlation between the PCBz and PCDF and the intermediate compound PCB have been investigated. The correlation between these compounds for the samples with higher toxicity is shown in Fig. 2.

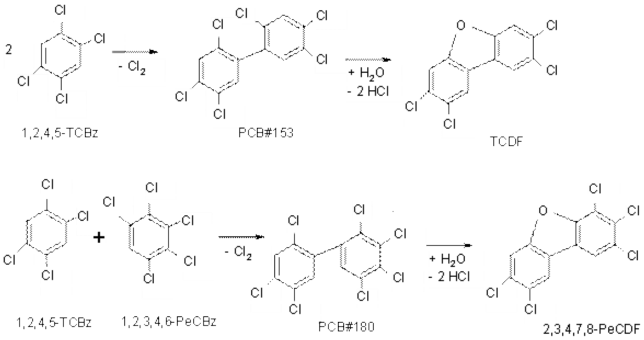
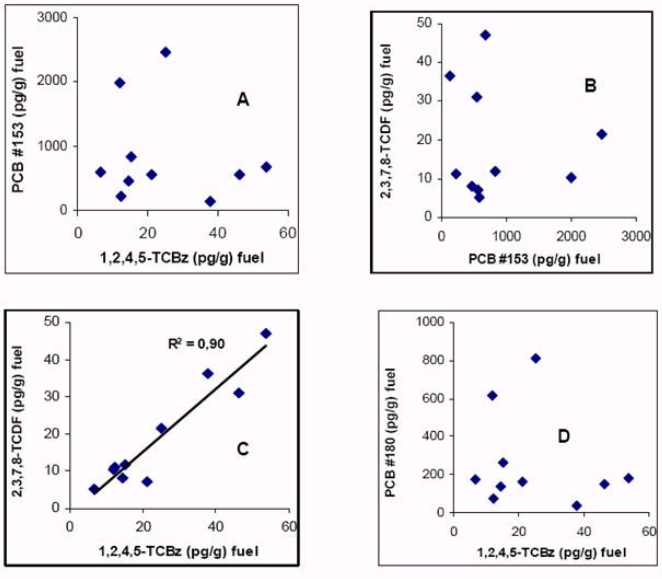


Fig.1 Scheme of TCDF and PeCDF formation



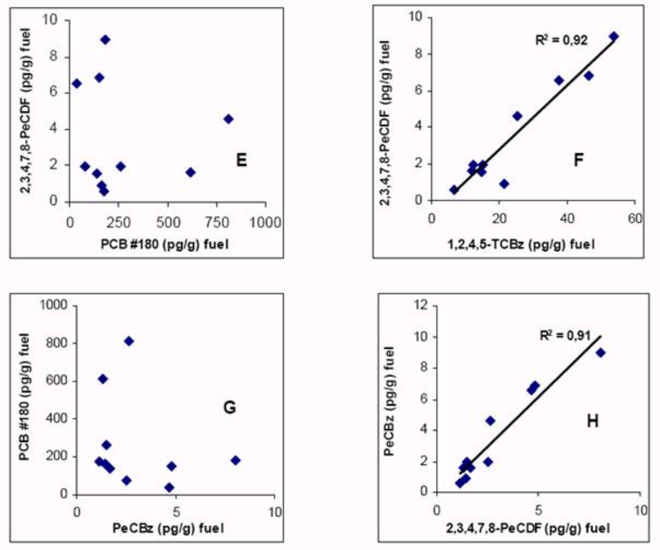


Fig. 2 Correlation between: PCB#153 and 1,2,4,5-TCBz (A); PCB#153 and 2,3,7,8-TCDF (B); 2,3,7,8-TCDF and 1,2,4,5-TCBz (C); PCB#180 and 1,2,4,5-TCBz (D); 2,3,4,7,8-PeCDF and PCB#180 (E); 2,3,4,7,8-PeCDF and 1,2,4,5-TCBz (F); PCB#180 and PeCBz (G); 2,3,4,7,8-PeCDF an PeCBz (H).

According to Fig. 2 the concentration profile I-TEQ value of the toxic 2,3,7,8-TCDF congener is quantitatively similar to those of 1,2,4,5-TCBz. A fairly good relationship is obtained for PeCBz and 2,3,4,7,8-PeCDF. The latter correlated also very good with 1,2,4,5-TCBz. However, the PCB congeners are poorly correlated with PCDF and PCBz congeners for the samples with higher toxicity. According to the precursor theory of PCDD/F formation a fusion of two chlorophenyl radicals result in PCB compounds by two different dechlorination reactions (Fig. 2). In later steps that molecules can be oxidized and are thus potential precursors of PCDF. However, for the proposed mechanistic pathway of PCDF formation no correlation is found neither for group of samples between PCB homologues and nor for PCDD/F or PCBz homologues.

In addition another formation pathway for PCDD/F has been suggested leading via chlorophenols [10]. A main pathway for higher chlorinated PCDF may lead via these intermediates to the break down of the relationship. It is suggested that 1,2,4,5-TCBz is hydrolyzed to 2,3,4-trichlorophenol, which reacts with another molecule 1,2,4,5-TCBz under elimination of H_2O and Cl_2 from the ortho position.

The samples with high inhibitory outcome and low toxicity show no any relationship between the PCDF, PCB and PCBz tetra and pentachlorinated congeners. An explanation could be that inhibition result in breaking down the quiasi- stationary equilibrium among various classes of chloroaromatic compounds because the inhibitors are blocking catalytic active sites of the fly ash [4].

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