

THE ROLE OF HCl, Cl<sub>2</sub>, AND Cl RADICALS IN THE FAST, IN-FLIGHT FORMATION OF PCDDs AND PCDFs

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### Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in municipal solid waste (MSW) is not completely understood since the formation takes place in a very complex chemical environment. It is yet to be determined whether these toxic compounds are formed by smaller chlorinated hydrocarbons (precursors), and/or from larger aromatic hydrocarbons that are subsequently chlorinated. Experiments conducted by Wikström and Marklund<sup>1</sup> showed that additional secondary chlorination reactions of chlorinated and non-chlorinated organic compounds, such as PCDDs/Fs, polychlorinated biphenyls (PCBs), polychlorinated phenols (PCPhs), and polychlorinated benzenes (PCBzs), predominate over *de novo* synthesis reactions (from fly-ash-bound carbon) at low temperatures (650-200°C). Many questions, however, still need to be answered such as: How are the organic compounds chlorinated? And what parameter controls the chlorination? Most of the chlorine present in the flue gases is hydrogen chloride (HCl), which is a relatively poor chlorinating agent. Experiments by Procaccini<sup>2</sup> confirmed that HCl does not directly participate in the formation of chlorinated organic species, but undergoes reactions with oxidizing radicals [e.g., hydroxy (OH•), oxygen (O•), hydrogen (H•), hydroperoxy (HO<sub>2</sub>•)] from the combustion environment to form chlorine (Cl) radicals. The Cl radicals participate in subsequent hydrogen (H) abstraction and/or radical reactions with hydrocarbons to form chlorinated organics and HCl. The speciation between HCl, chlorine (Cl<sub>2</sub>), and Cl radical and interactions with other radicals in combustion processes are relatively well known<sup>3</sup>, and good agreement between theoretical and experimental results has been obtained for specific systems<sup>2</sup>. The actual amount of Cl radicals in the flue gas depends upon the combustion conditions, such as high reaction temperatures and fast quenching of the hot flue gas, as well as high oxygen or oxidizing radical concentrations (OH•, O•, HO<sub>2</sub>•)<sup>4</sup>. Results reported by Procaccini<sup>2</sup> and Gullett *et al.*<sup>4</sup> showed that the formation of PCBzs and PCPhs from benzene was highly affected by the amounts of Cl radicals and only slightly by the amount of Cl<sub>2</sub> present in the flue gas. The aim of this study is to investigate the formation of PCDDs/Fs during different combustion environments (*i.e.*, with and without flame) which give rise to different radical concentrations and hence different concentrations of Cl radicals in the flue gas.

### Methods and Materials

Experiments were performed in an Entrained Flow Reactor (EFR), consisting of a horizontal premixed flame burner inserted into a 22 mm I.D. quartz tube in series with a 15 mm I.D. vertical

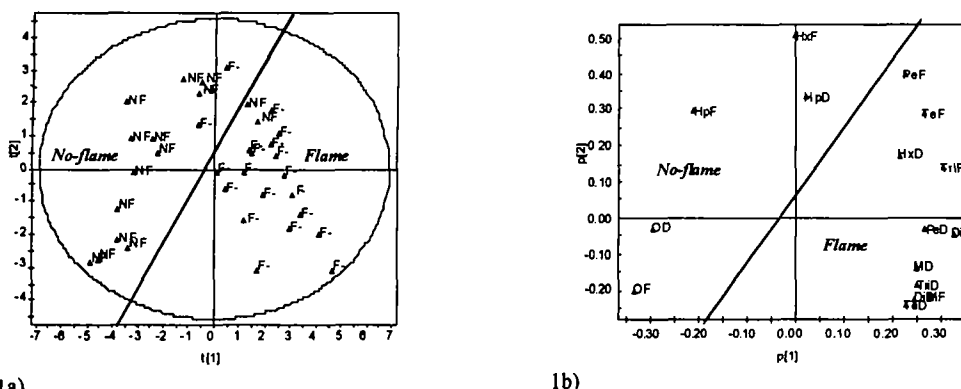
<sup>#</sup> This work was performed at the U.S. EPA/NRMRL through participation in the ORISE post-doctoral research program.

quartz tube reactor. The system was electrically heated by four Lindberg furnaces, one for the horizontal combustor and the additional three for the vertical reactor. The temperature profile in the system was controlled by the Lindberg furnaces and was independent of the presence or absence of the combustion flame. The experiments were performed at 1000 °C in the horizontal combustor and with a quenched temperature profile between 650 and 240 °C in the vertical reactor to simulate post-combustion temperature conditions. The premixed flame burner was supplied with methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), or nitrogen (no fuel) in different mixtures of oxygen and nitrogen. The experiments were performed with the same amount of hydrogen added to the system independent of fuel (CH<sub>4</sub> or H<sub>2</sub>) employed. A preheated gas mixture of N<sub>2</sub> and 10% Cl<sub>2</sub> was added concentric to the flame at a flow rate of 25 mL/min, corresponding to approximately 250 ppm Cl<sub>2</sub> in the reactor. The total gas flow was 12 L/min, producing a residence time of 1.0 s in the vertical reactor and a total residence time of 1.6 s. Fly ash particles (<105 µm) were fed to the vertical reactor by a carrier gas (N<sub>2</sub>) with a feed rate of 1 g of ash per hour (in total, 2 g). Two fly ashes were employed in these experiments: EPA-AR (as-received) collected from the electrostatic precipitator of a grate-fired municipal solid waste incinerator, and a derivate fly ash designated as EPA-EX (extracted). EPA-EX fly ash was prepared by extracting AR fly ash with toluene over 48 h and then heating to 500 °C in an N<sub>2</sub> atmosphere for 24 h. This procedure resulted in a minimization of organic compounds (PCDDs/Fs) on the fly ash. The total amount of carbon in the EPA-AR was reduced from 1.30 to 0.52%; however, other parameters such as weight loss in oxygen (14%), amount of Cl (6.3%), and metals (copper 0.16%), remained unchanged. As a consequence, the extraction and heating process of the fly ash appears to have minor if not negligible effect on the organic macromolecular structure. A total of 35 experiments, 20 with the flame (9 with AR- and 11 with EX- ash) and 15 without the flame (9 with AR- and 6 with EX- ash), were performed. To evaluate the results of the experimental work, the theoretical concentrations of HCl, Cl, and Cl<sub>2</sub> in the horizontal combustor and the vertical reactor were simulated using REKINET, a program based on CHEMKIN-II<sup>5</sup> to solve homogeneous gas-phase kinetics. A chlorocombustion mechanism originally compiled by Ho *et al.*<sup>3</sup> and also employed by Procaccini<sup>2</sup> was used in the simulations.

### Results and Discussion

No significant differences between the PCDD/F yields of the two different ashes could be discerned within the data (AR: 120-3700, EX: 180-2000 ng/dscm). Distinctly higher yields were observed between the no-flame results (1200-3700 ng/dscm) compared to the flame results (120-500 ng/dscm). The experiments performed with H<sub>2</sub> flame caused higher PCDD/F levels than the CH<sub>4</sub> flame experiments. These observations suggest that the carbon present in the EX and AR ash was able to act as a major carbon source for the formation of PCDDs/Fs in the experiments. The PCDD/F homologue profiles for the 35 experiments were further statistically evaluated with Principal Component Analysis (PCA). The PCA data matrix consists of 35 objects (the number of experiments) and 16 variables (the relative homologue concentration within each experiment). The homologue levels were transformed into relative levels [mono-CDF (MF) = ng of mono-CDF/Σ ng of mono- to octa- CDF] to focus on the changes in homologue profiles independent of variations in total PCDD/F levels. The PCA model consists of four components, with a model validity of R<sup>2</sup>=0.88 and Q<sup>2</sup>=0.63 (Q<sup>2</sup> represents the model prediction capacity). The first component versus the second component from the analysis is displayed in Figures 1a and 1b. A division into one field with experiments performed at flame condition (F) to the lower right and one with no-flame (NF) to the upper left can be discerned in the score plot (Figure 1a). No significant differences within the homologue profiles between the two fly ashes (EX and AR) and the two fuels used (CH<sub>4</sub> and H<sub>2</sub>) could be discerned within the data set. The loading plot in Figure 1b reveals that experiments performed at no-flame conditions show significantly higher relative levels of the higher chlorinated

homologues (e.g., OD, OF, HpF) compared to the flame experiments which appear to produce mainly the lower chlorinated homologues (e.g., M- to Pe- D/F).



1a)

1b)

Figures 1a and 1b. The score- and loading-plot from the PCA evaluation of the homologue profiles, respectively. The first component explains 48 % of the variation in the data and additionally 22 % is explained by the second component. The corresponding  $Q^2$  values for the first and the second components are 0.37 and 0.28, respectively. Notation: mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa- PCDD/F = M-, Di-, Tri-, Te-, Pe-, Hx-, Hp-, O- D/F, respectively.

The theoretical gas-phase compositions in the experimental reactor were simulated using REKINET/CHEMKIN-II calculation at four different conditions:  $\text{Cl}_2$ /flame,  $\text{Cl}_2$ /no-flame, HCl/flame, and HCl/no-flame. The theoretical amounts of Cl radicals in the flue gas at the different conditions are displayed in Figure 2. Without the flame environment (for both  $\text{Cl}_2$  and HCl), significant levels of Cl radicals ( $>18$  ppm) persist in the gas phase, decreasing to around 1.5 ppm in the last second of the vertical reactor due to recombination of Cl radicals to  $\text{Cl}_2$ . When the system operates with combustion of  $\text{CH}_4$  or  $\text{H}_2$ , the majority of the added  $\text{Cl}_2$  is converted to HCl due to reactions with  $\text{H}_2$ , H, and OH from the flame. For this case, less than 1.5 ppm of Cl radicals persist, dropping to around 0.05. In either the flame or no-flame case, the levels of Cl radicals in the flue gas are still high compared to the levels of PCDDs/Fs and so their influence on the yields of PCDDs/Fs is worth considering. Figure 3 presents the total measured amount of PCDDs/Fs in 17 representative experiments versus the calculated Cl radical concentrations. The plot reveals that PCDD/F yields do in fact increase with increasing Cl radicals. These results and the predominance of the higher degree of chlorination in no-flame (high Cl radical) conditions from the PCA plots, imply that the presence of Cl radicals could be a critical influencing factor on chlorination and PCDD/F formation. Note that the flame also introduces other compounds (e.g.,  $\text{CO}_2$ , CO,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , H, OH,  $\text{HO}_2$ ) to the fly ash surface, which could enable competing reactions with the Cl radicals for reactions with the active carbon. It is important to determine whether the chlorine source (HCl or  $\text{Cl}_2$ ) or the flame environment has a greater impact on the PCDD/F formation and chlorination profiles. Figure 4 shows the differences within the PCDD/F homologues between three different experimental conditions:  $\text{Cl}_2$ /no-flame, HCl/no-flame, and  $\text{Cl}_2$ /flame. As the PCA results conclude, the profiles shown in Figure 4 for the two no-flame conditions reveal a predominance of the higher chlorinated homologues, regardless of the original chlorine source. This implies that the rate of formation (Figure 3) and the degree of chlorination (Figure 4) of the PCDDs/Fs are significantly affected by the presence/absence of a flame, through the amount of Cl radicals present (consistent also with secondary organic chlorination<sup>1</sup>). The most significant difference in the calculated amounts of Cl radicals between the three experimental conditions is noticed within the first 300 ms in the vertical reactor, suggesting that the reactions between the fly ash carbon and the Cl radical are very fast.

# FORMATION AND SOURCES - POSTERS

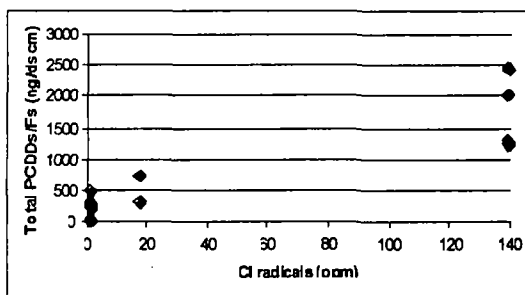
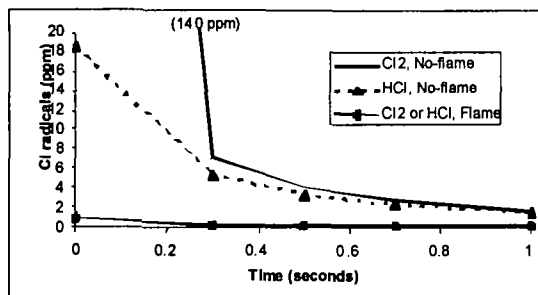


Figure 2. CHEMKIN calculation of Cl radical concentrations present along the vertical reactor after 0.7 s in the horizontal reactor at 1000 °C. Four different experimental conditions compared.

Figure 3. Total amount of PCDDs/Fs vs. theoretical amount of Cl radicals in the flue gas (N=17, some points obscured).

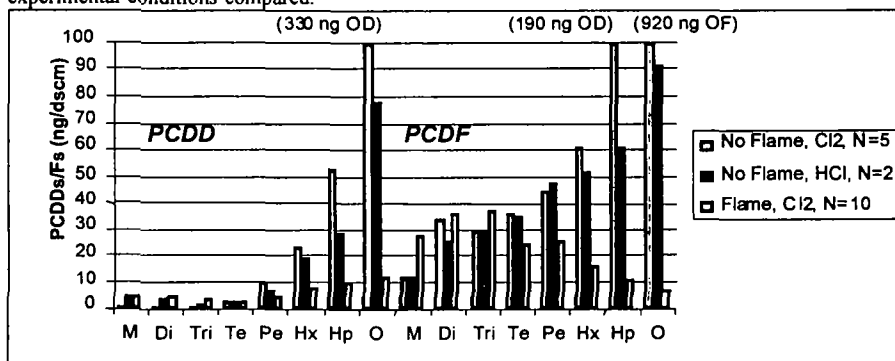


Figure 4. The average PCDD/F homologues profiles at three different combustion conditions, N=number of runs.

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## References

1. Wikström E. and Marklund S. (2000) *Environ. Sci. Technol.* 34, 604.
2. Procaccini C. (1999), (*Ph. D. Thesis*), Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA.
3. Ho W.D., Yu Q. and Bozzelli J.W. (1992) *Combustion Sci. Technol.* 85, 23.
4. Gullett B. K., Sarofim A.F., Smith K. A. and Procaccini C. (2000) *Trans IChemE*, 78, 47.
5. Kee R.J., Rupley F.M. and Miller J.A. (1989) CHEMKIN-II: A FORTRAN, SAND89-8009, Sandia National Laboratories, Albuquerque, NM, USA.