

# FORMATION AND SOURCES II

## RATE AND CARBON SOURCE FOR IN-FLIGHT PCDD AND PCDF FORMATION

Brian K. Gullett<sup>1</sup>, Elmar R. Altwicker<sup>2</sup>, Abderahmane Touati<sup>3</sup>

<sup>1</sup>U.S. Environmental Protection Agency, National Risk Management Research Laboratory (MD-65), Research Triangle Park, NC 27711, USA, gullett.brian@epa.gov

<sup>2</sup>Rensselaer Polytechnic Institute, Department of Chemical Engineering, Troy, NY 12180, USA

<sup>3</sup>ARCADIS Geraghty & Miller, P.O. Box 13109, Research Triangle Park, NC 27709, USA

### Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) are formed in trace quantities in combustion processes. Validation of the PCDD/F formation mechanism, through explanation of field-observed yields, is significantly hampered by the inability to simulate in the laboratory the complex and overlapping chemical, physical, and thermal processes that occur in field situations. Indeed, extensive laboratory efforts on the *de novo* synthesis mechanism<sup>1</sup> and the precursor mechanism<sup>2-5</sup> have not yielded mechanistic rates that are sufficient to explain sampled concentrations of PCDDs/Fs in field units.<sup>6</sup>

Some experimental results have demonstrated elevated rates of formation in combustion laboratory experiments. Fångmark et al.<sup>7</sup> reported over 1000 ng/m<sup>3</sup> within 0.8 to 3 s during combustion of a pelletized, refuse-derived fuel in a fluidized bed. Gullett et al.<sup>8,9</sup> obtained PCDD/F formation that exceeded 10,000 ng/m<sup>3</sup> and 1,000 ng/g/s via injection of field-collected municipal waste combustor (MWC) fly ash into a controlled temperature and gas environment. These latter two studies showed rates that are sufficient to explain field-observed sampling results. However, it is not clear if these higher rates are due to more realistic experimental simulations or to fuel carbon's contributing to the PCDD/F structures. The work reported here presents initial results from a laboratory flow reactor study on PCDD/F formation rates and carbon sources.

### Method

Experiments were conducted in the Entrained Flow Reactor (EFR), an electrically heated, vertical reactor 3.09 m in length with a bulk gas residence time of about 1 to 3 s. Preheated gases are combined with fly ash in a nitrogen (N<sub>2</sub>) carrier gas at the top of the reactor. An electrically heated (1000 °C), horizontal, premixed flame burner can optionally supply combustion products to the vertical EFR. Concentric to the flame zone, chlorine (Cl<sub>2</sub>) or hydrogen chloride (HCl) in N<sub>2</sub> can be introduced. Methane (CH<sub>4</sub>) or hydrogen (H<sub>2</sub>) fuels in oxygen (O<sub>2</sub>) provide an optional source of potential carbon (C)- and/or hydrogen (H)-based reactants. The EFR can also be operated without the flame burner because the temperature profile of the electrically heated EFR is independent of the presence or absence of a flame. This feature is critical for tests in which the burner will not act as a source of C and for tests with varying CH<sub>4</sub> feed rate. For this work, the EFR is operated in a quenched mode (650 - 240 °C) such that the fly ash particles will pass through the common PCDD/F formation window (~350 °C). Sieved (< 105 μm) fly ash particles are fed with a fluidized bed feeder at a rate of 1 (± 0.10) g/h. Rinses of the reactor walls showed minimal wall deposition, about 10% of the collected fly ash mass, for which analyses showed mass-

## FORMATION AND SOURCES II

proportional amounts of PCDDs/Fs. Gas sampling tests after fly ash feeding showed that this minor amount of deposited fly ash was unreactive toward additional formation.

The fly ash to be tested in these experiments was from a single U.S. MWC and termed "EPA Fly Ash." The as-received fly ash (EPA AR) was treated to minimize the presence of any organic and fixed C source by placing the fly ash in flowing air at 500 °C for 24 h. The resultant oxidized fly ash ("OX") has a C content of 0.201 wt % compared to the EPA AR fly ash at 1.305 wt %. The inorganic halogens as chlorine (Cl) were 6.41 and 6.30 wt % for AR and OX, respectively. Elemental analysis showed little change, if any, in the metals concentrations due to production of OX. For example, the AR and OX concentrations for copper (Cu) were 0.16 and 0.17 wt %, respectively, and those for iron (Fe) were 0.91 and 1.11 wt %, respectively. This suggests that the OX thermal treatment technique was effective at reducing the C concentration while minimizing the impact on potential metal catalysts.

Fuel was burned in the horizontal burner at a range of equivalence ratios, denoted  $\phi_H$ . The fuel and oxidizer input rate determined  $\phi_H$ . The vertical EFR has an optional air input port after the horizontal burner, which allows for testing fly ash reactivity in oxidant atmospheres distinctive from the burner. The equivalence ratio in the vertical EFR is termed  $\phi_V$  and is calculated from the fuel input rate and the total (flame burner + EFR) oxygen input. In this manner,  $\phi_H \geq \phi_V$ , and a fuel-rich burner can supply partially combusted species to fly ash entrained in an oxygenated atmosphere.

The entire EFR gas volume was sampled and analyzed using methods described more fully elsewhere.<sup>10</sup> PCDD/F formation rates are expressed as mass of mono- to octa-CDD/F formation (unless otherwise noted) per g of fly ash collected per s of residence time.

Fixed bed, *de novo* type experiments were also conducted, using a mixture of 0.5 g fly ash mixed with 0.5 g glass beads, held at 299 °C for 60 min in 10% O<sub>2</sub>/N<sub>2</sub> at 91-94 mL/min followed by a toluene cold trap.

### Results and Discussion

Short time EFR tests in air to determine the reactivity of OX in the absence of a flame and Cl source yielded 36 and 37 ng/g/s. This suggests that even a relatively C-free fly ash (0.201%) still contains sufficient reactive C (by a factor of 10<sup>5</sup>) and Cl to form PCDD/F in a short time, quenched regime. The tetra- to octa-CDD/F EFR results (Fig. 1, bar "OX, AIR") can be directly compared with fixed bed, isothermal (299 °C) tests (*de novo* type) with the same OX fly ash and a similar atmosphere (Fig. 1, bar "x 100: OX, AIR"). The short time, maximum EFR rate was about 18 ng/g/s (tetra- to octa-CDD/F) based on 1.14 s residence time while the fixed bed test yielded only about 0.1 ng/g/s (tetra- to octa-CDD/F) based on 60 min of reaction time. The EFR formation rates are significantly higher (over 2 orders of magnitude) than the same fly ash in an isothermal atmosphere. However, these rates are not directly comparable, as the fixed bed rate has been shown to decline significantly with time. Blaha and Hagenmaier<sup>11</sup> found rates of formation of about 7, 3, and 0.3 ng/g/s for run durations of 1, 5, and 30 mins, respectively. Extrapolating these differences to compare the quenched temperature, 1.14 s EFR rates with the 60 min fixed bed rates is tenuous, but may explain the large difference in OX yields observed between our short time, in-flight versus fixed bed tests.

The effect of Cl<sub>2</sub> addition (225 ppm in N<sub>2</sub>) with air to the short-time, in-flight OX tests (above) resulted in increased PCDD/F yields to 58, 129, and 463 ng/g/s (Fig. 1, "OX, Cl<sub>2</sub>, AIR"). Note that the Cl<sub>2</sub> was added to the horizontal flame burner while no fuel was being burned. These

## FORMATION AND SOURCES II

results demonstrate that the presence of added  $\text{Cl}_2$  may accelerate chlorination of surface-bound C in a short time, quenched regime, forming PCDD/F, although conclusions must be tempered by the wide range of the data. The presence of  $\text{Cl}_2$ , or the products of  $\text{Cl}_2$  in a high temperature ( $1000^\circ\text{C}$ ) environment, may contribute to additional chlorination of the fly ash C structure, above that observed for the nascent-Cl-only runs (first results, mentioned above). Thus,  $\text{Cl}_2$  may result in faster formation (higher yields) of the PCDD/F products. When the air is replaced with  $\text{N}_2$ , the formation of PCDD/F from the nascent C at this short residence time condition does not require the presence of gaseous  $\text{O}_2$ . Understanding these results requires consideration of the fate of  $\text{Cl}_2$ , both species and concentration, in this environment.

To test the effect of a flame source on OX reactivity, tests with a premixed  $\text{H}_2/\text{O}_2$  flame in the presence of  $\approx 400$  ppm  $\text{Cl}_2$  were run which resulted in PCDD/F formation rates of 10, 100, 315, and 331 ng/g/s (Fig. 1, "OX,  $\text{Cl}_2$ ,  $\text{H}_2$ "). These results are not clearly distinctive from those of  $\text{Cl}_2$  in air (above). This suggests that any  $\text{H}_2$ -based flame products, such as hydrogen radicals ( $\text{H}\cdot$ ), hydroxyl radicals ( $\text{HO}\cdot$ ), and water ( $\text{H}_2\text{O}$ ), as well as any effect they might have on the Cl species and concentrations, do not make a significant difference in fly ash C reactivity.

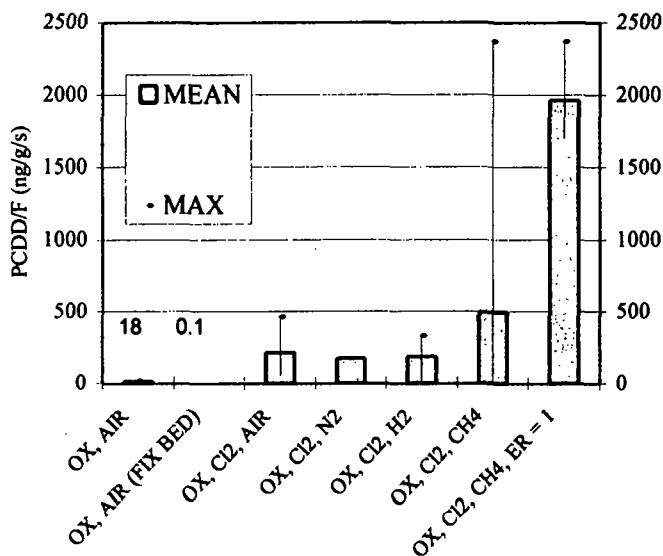


Figure 1. Formation rate of mono- to octa-CDD/F (ng/g/s) by OX fly ash. First two bars are tetra- to octa-PCDD/F for the PCDD/F for the EFR and the  $299^\circ\text{C}$  fixed bed reactor, respectively. Values indicate means. ER indicates optimum equivalence ratio.

## FORMATION AND SOURCES II

CH<sub>4</sub>/O<sub>2</sub> premixed flames in the presence of  $\approx$  400-800 ppm Cl<sub>2</sub> were run to test the effect of a carbonaceous flame source on OX reactivity. PCDD/F rates ranged from 0 to 2369 ng/g/s (Fig. 1, "OX, Cl<sub>2</sub>, CH<sub>4</sub>"). Very high PCDD/F yields (>1700 ng/g/s) were achieved during specific conditions in three tests in which  $\phi_H$  was slightly rich (1.031 to 1.074) and  $\phi_V$ , due to the introduction of post-combustion air, was slightly lean (0.95 to 0.98). These three short time, in-flight, flame-presence, OX tests resulted in a rate of formation that was about 20 times faster than those of the comparable non-CH<sub>4</sub>, non-Cl<sub>2</sub>, tests and are sufficiently fast to explain field-observed emissions. These OX, Cl<sub>2</sub>, CH<sub>4</sub> yields are exceptionally high and confirm that the presence of a CH<sub>4</sub> flame, under certain conditions, can result in increased PCDD/F formation. In all other cases where the fuel was combusted lean at  $\phi_H < 1$  or rich at  $\phi_H > 1.1$ , regardless of the value of  $\phi_V$  (though it is required that  $\phi_H \geq \phi_V$ ), PCDD/F yields were low. If combustion was sufficiently fuel rich and was accompanied by introduction of post-combustion air, the fuel flammability limit was reached and the mixture reignited. This resulted in reduced carbon monoxide (CO) levels and low PCDD/F formation. The specificity of  $\phi_H$  and  $\phi_V$  regimes in which PCDD/F yields are affected suggests that the species that are responsible for promoting PCDD/F formation are extremely sensitive to fuel combustion conditions. The effect of a flame source may also extend to fixed bed tests: propene combustion products with added HCl passed over MWC fly ash<sup>12</sup> resulted in a rate of about 20 ng/g/s, much higher than rates reported earlier<sup>11</sup> in this paper.

The further increase in PCDD/F formation rates with the addition of a CH<sub>4</sub> flame to Cl<sub>2</sub>, and the critical dependence of these reactions on the equivalence ratio regime, suggest that careful study of the role of species generated by CH<sub>4</sub> flames, in the presence of a Cl source, will yield valuable insights into the formation mechanism. The CH<sub>4</sub> effect may be to either 1) supply additional C-based reactants for incorporation into the PCDD/F structures or 2) affect the concentration and species of the chlorinating agent.

### References

- 1 Stieglitz, L., and Vogg, H. (1987) *Chemosphere* 16, 1917-1922.
- 2 Shaub, W. M., and Tsang, W. (1983) *Environ. Sci. Technol.* 17(12), 721-730.
- 3 Sidhu, W. S., Maqsood, L., Dellinger, B., and Mascolo, G. (1995) *Combust. Flame* 100, 11.
- 4 Dickson, L.C., and Karasek, F.W. (1987) *J. Chromatogr.* 389, 127-137.
- 5 Huang, H., and Buekens, A. (1995) *Chemosphere* 31(9), 4099-4117.
- 6 Altwicker, E. (1996) *J. Haz Materials* 47, 137-161.
- 7 Fängmark, I., van Bavel, B., Marklund, S., Strömberg, B., Berge, N., and Rappe, C. (1993) *Environ. Sci. Technol.* 27: 1602-1610.
- 8 Gullett, B. K., Lemieux, P. M., and Dunn, J. E. (1994) *Environ. Sci. Technol.* 28, 107-118.
- 9 Gullett, B. K., and Raghunathan, K. (1997) *Chemosphere* 34 (5-7), 1027-1032.
- 10 Gullett, B.K., Ryan, J.V., and Tabor, D. (1999) *Organohalogen Compounds* 40, 121-124.
- 11 Blaha, J., and Hagenmaier, H. (1995) *Organohalogen Compounds* 23, 403-406.
- 12 Jarmohamed, W., and Mulder, P. (1994) *Organohalogen Compounds* 20, 1911-1917.