

FORMATION AND SOURCES I

PCDD/F FORMATION RATES FROM FLY ASH AND METHANE COMBUSTION CARBON SOURCES

Brian Gullett¹, Elmar Altwicker², Evalena Wikström^{1,#}, Abderrahmane Touati³

¹U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, MD-65, Research Triangle Park, NC 27711, USA

²Rensselaer Polytechnic Institute, Department of Chemical Engineering, Troy, NY 12180, USA

³ARCADIS Geraghty & Miller, Inc., P.O. Box 13109, Research Triangle Park, NC 27709, USA

[#]Appointment through Oak Ridge Institute for Science and Education postdoctoral program

Introduction

Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (hereafter collectively termed APCDD,Fs@) are formed in trace quantities in combustion processes via two primary mechanisms: so-called *de novo* synthesis in which PCDD,Fs are formed from non-extractable carbon (C) structures that are basically dissimilar to the final product PCDD,F¹; and precursor formation/reactions^{2,3} via aryl structures derived from either incomplete aromatic oxidation or cyclization of hydrocarbon fragments.

Extensive laboratory efforts on the *de novo* synthesis¹ and precursor mechanisms²⁻⁴ have not yielded mechanistic rates, homologue profiles, and PCDD/F ratios that satisfactorily reflect sampled concentrations of PCDD,Fs in field units⁵. The observed *de novo* rates⁶ at the optimum temperature (200 to 400 °C) vary from about 0.2 to 2 ng PCDD,F (tetra- to octa-chlorinated) per g of fly ash per s of solid-phase residence time (ng/g_{FA}Xs), which is still more than 2 to 3 orders of magnitude below apparent incinerator rates⁵ of about 400-800 ng/g_{FA}Xs⁷. Entrained flow combustor tests^{8,9} have obtained rates > 1,000 ng/g_{FA}Xs with homologue profiles and PCDD/F ratios more closely mimicking those observed in field units, but they are still insufficient to adequately discern distinctive C source mechanisms and, hence, provide methods of formation prevention. In order to more adequately simulate and control the conditions under which PCDD,F formation is expected in combustion, a flow reactor was built to test these mechanistic hypotheses in a reasonably realistic simulation. This electrically heated, controlled-atmosphere system with an optional fuel burner was used with injection of field-sampled fly ash in an attempt to answer questions regarding the origin of the PCDD,F C and, in a companion paper, the role and fate of chlorine on PCDD,F formation¹⁰.

FORMATION AND SOURCES I

Methods and Materials

Experiments were conducted in the Entrained Flow Reactor (EFR), an electrically heated, vertical reactor 3.09 m long and with a 3-cm ID and a bulk gas residence time of about 1 to 2 s. Preheated gases are combined with fly ash in a nitrogen (N_2) carrier gas and injected at the top of the reactor. An optional, electrically heated (1000 °C), horizontal, premixed flame burner can supply combustion products to the vertical EFR. Concentric to the flame zone, molecular chlorine (Cl_2) or hydrogen chloride (HCl) in N_2 can be introduced. Combustion of methane (CH_4) or hydrogen (H_2) fuels in oxygen (O_2) can provide a source of potential C- and/or hydrogen (H)-based reactants. The vertical EFR has an air input port after the horizontal burner, which allows for testing fly ash reactivity in oxidizing atmospheres (ϕ_v) distinctive from the burner (ϕ_H). The EFR can also be operated without the flame 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_4 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-proportional amounts of PCDD,Fs. Gas sampling tests after fly ash feeding showed that this minor amount of deposited fly ash was unreactive toward additional formation. The gases exiting the EFR are sampled and analyzed via modified EPA methods, detailed elsewhere⁷, for mono- to octa-CDD,F. Fixed bed, *de novo* 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_2/N_2 at 91-94 mL/min followed by a toluene cold trap.

The three fly ashes used in these experiments and others¹¹ were derived from a single U.S. Municipal Waste Combustor (MWC) and termed AEPA Fly Ash.® The as-received fly ash (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, resulting in a second, oxidized fly ash (OX) (see also Ref. 12). Another fly ash, to simulate an extracted fly ash without surface-bound organic C (EX), was treated similarly but in flowing N_2 , rather than air. Similar treatments have shown that this method retains the fly ash reactivity to chlorophenol condensation formation of PCDD¹³. The C contents for AR, EX, and OX, respectively, were 1.3, 0.5, and 0.2 wt %. The bulk, not surface, Cl and copper (Cu) contents were invariant at 6.5 and 0.17 wt %, respectively, showing little change, if any, due to production of OX or EX. Nascent total mono- to octa-CDD,F concentrations for AR, EX, and OX were 740, 20, and 1 ng/g, respectively. Based on the ability of a second, distinctive as-received ash with low nascent PCDD,F concentration (10 ng/g) to achieve similar rates of PCDD,F formation as AR (not shown), this work makes the preliminary assumption that nascent PCDD,F levels under these test conditions do not substantially contribute to resulting rates of formation.

FORMATION AND SOURCES I

Results and Discussion

Tests with the three fly ashes as the only source of C (in the absence of a flame) suggest the ability of the nascent C to contribute to PCDD,F formation in a short-time, quenched reactor. Table I shows average rates of all three fly ashes in the absence (N₂) or presence of added O₂ (AIR). Fly ash rates are AR > EX > OX, appearing proportional to the amount of C in the nascent fly ash, and are significantly enhanced by the presence of O₂. The non-zero formation from EX and OX suggests that extractable organic precursors are not necessary for formation: sufficient C is found within the bound carbonaceous matrix, demonstrating classic *de novo* synthesis. The significant formation rates in N₂ (averaging 154 ng/gXs for AR) suggest that the O species deemed necessary for *de novo* formation¹⁴ can be derived, in part, from the fly ash itself. That O appears to proportionately enhance rates (from those in a N₂ atmosphere) suggests that the O mechanism of action is related to the C present in the ash. Likewise, sufficient Cl present for *de novo* formation is also present in the fly ash.

The highest rate, from AR in air, was 850 ng/gXs, sufficient to explain most field-observed concentrations. The comparative inactivity of OX (36 ng/gXs) may be directly related to its relatively low C content or to some physical alteration of the surface; bulk Cl and Cu (as a catalyst) were not affected by OX production.

The addition of an average of 500 ppm Cl₂ at 1000 °C during the N₂ and AIR conditions results in substantial increases in reactivity for all three fly ashes (AR □ EX > OX). Substantial PCDD,F formation (> 2500 ng/gXs, for AR and EX) can be expected even during non-oxidizing conditions. Since no distinction is observed in rates between the N₂ and AIR conditions, this suggests that the effect of O₂ addition does not affect the promotion by Cl species.

The potential contribution of fuel C to PCDD,F was tested by adding product gases from a CH₄ burner prior to the fly ash injection. When AR results (265 ng/gXs) are compared with those from N₂ (3172 ng/gXs) or AIR (3,077 ng/gXs), NF (no flame) conditions, it is clear that under these flame conditions, rates are significantly reduced. This observed effect is likely independent of the low O₂ levels, given the high rates from N₂, NF runs. More likely, under our conditions the CH₄ flame products affect the Cl reactivity, mimicking the low rates from AR, N₂ (154 ng/gXs). The flame presence also reduced AR reactivity below that observed solely from the fly-ash-bound Cl (AR AIR, 636 ng/gXs). Thus, flame species may affect both the gas-phase chlorination agent and, through potential reduction of O₂, the surface reactivity¹⁵.

The rates of the EX runs in the presence of CH₄ combustion and Cl₂ cover a wider range (398 ng/gXs, ∇ 540 σ, not shown) than those of AR (265 ng/gXs, ∇ 92 σ). Reactivity appears to be related to the burner operation: as φ_H declines, the average rate increases significantly (a comparable φ_H range for AR was not done). The EX runs suggest that sufficient O₂ can overcome the deleterious effect of the flame presence on Cl reactivity. Since we earlier determined that O₂ and the reactive Cl species did not interact, it is possible that some other flame product may act as an intermediate reactant, affecting the Cl reactivity. Of AR and EX tests in CH₄, the highest rates (> 1,000 ng/g_{FA}§s) were achieved at low CO (< 10 ppm) and excess O₂. This is contrary to typical expectations of high

FORMATION AND SOURCES I

PCDD,F formation during poor combustion. Tests with a H₂ flame show similar suppression of AR and EX reactivity (from AIR tests) as did CH₄. Likewise, EX runs with low CO (< 15 ppm) show higher rates (> 250 ng/g_{FA}Ⓐs) than at high CO.

In view of OX=s heretofore extremely low rates, it is surprising to find three runs with rates at 1,975 ng/g_{FA}Ⓐs (σ = 323). These three runs have CH₄ burner characteristics of φ_H □ 1.02 (based on gas flow settings) and EFR φ_V □ 0.97 (based on post-EFR O₂ measurements) due to post-flame air addition), such that CO is low (< 15 ppm) and 0.4 < O₂ < 0.9 %. These high rates have been difficult to repeat, likely due to the sensitivity of the burner operated near φ_H = 1¹⁶.

The in-flight *de novo* rates (AIR) for AR, EX, and OX are 636, 249, and 36 ng/g_{FA}Ⓐs, respectively, and are considerably higher than those using the same fly ash in a fixed bed (0.72, 0.06, and 0.11 ng/g_{FA}Ⓐs for AR, EX, and OX, respectively, tetra- to octa-CDD,F only) and begin to approach magnitudes that can explain field-observed levels. The long-time, fixed-bed results are not true indicators of reaction rate: extrapolation of fixed bed tests¹⁷ of 1, 2.5, 5, and 30 min duration (model fly ash, 300 °C, air at 120 mL/min) to the EFR residence time (1.14 s) suggests a formation rate of approximately 300 ng/g_{FA}Ⓐs, within the range observed here.

The effects of these run condition changes can be described through a global rate expression for *de novo* PCDD,F formation:

$$d(\text{PCDD,F})/t = k [\text{Cl}_s]^m [\text{C}_s]^n [\text{O}_g]^o [\text{Cl}_g]^p$$

which was evaluated against the AIR data to derive the fly ash carbon content reaction order $n = 1.49 \pm 0.15$ s.e. (N=6). Similarly, and assuming the surface-bound Cl effect is constant for all three ash types, evaluating the non-flame data results in an order p for the Cl₂ gas effect of about 0.46 ± 0.08 s.e. (using all 18 values of N₂ and AIR data, excluding OX). Likewise, the paired AR and EX data were evaluated for the order effect o of gaseous O₂, resulting in 0.14 and 0.38, respectively. Approximating o at 0.25 and assuming non-zero concentrations result in a global rate expression for *de novo* formation:

$$d(\text{PCDD,F})/t = k [\text{Cl}_s]^m [\text{C}_s]^{1.49} [\text{O}_g]^{0.25} [\text{Cl}_g]^{0.46}$$

The order dependency m of the fly ash Cl concentration and the temperature sensitivity of k have not been evaluated in this work.

While the fast, in-flight *de novo* rates validate the relevance of this mechanism for combustion units, the contribution of flame C has not been wholly addressed. Indeed, the extremely high rates (>1,900 ng/g_{OX} Xs), with three OX tests run at burner φ_H . 1 conditions suggest that flame-derived C precursors may contribute to PCDD,F formation or accelerate surface reactions¹⁶. If only the latter, then formation proceeds at a rate normalized by the OX C content, or 800,000 ng/g_CXs, approximately a 0.1% yield.

FORMATION AND SOURCES I

References

1. Stieglitz L. and Vogg H. (1987) Chemosphere 16, 1917.
2. Dickson L. and Karasek F. (1987) J. Chromatogr. 389, 127.
3. Froese K. and Hutzinger O. (1996) Environ. Sci. Technol. 30, 998.
4. Sidhu S., Maqsd L., Dellinger B. and Mascolo G. (1995) Combust. Flame 100, 11.
5. Altwicker E. and Milligan M. (1993) Chemosphere 27, 301.
6. Huang H. and Buekens A. (1995) Chemosphere 31, 4099.
7. Gullett B., Dunn J. and Raghunathan K. (2000) Environ. Sci. Technol. 34, 282.
8. Gullett B., Lemieux P. and Dunn J. (1994) Environ. Sci. Technol. 28, 107.
9. Gullett B. and Raghunathan K. (1997) Chemosphere 34, 1027.
10. Wikström E., Touati A., Telfer M. and Gullett B. (2001) Organohalogen Compd. (submitted).
11. Hell K., Stieglitz L., Bautz H., Will R. and Zwick G. (1999) Organohalogen Compd. 41, 165.
12. Albrecht I. and Karasek F. (1995) Organohalogen Compd. 23, 323.
13. Milligan, M. (1994) (Ph.D. Thesis), Rensselaer Polytechnic Institute, Troy, NY.
14. Addink R. and Olie W. (1993) Organohalogen Compd. 11, 355.
15. Wikström E., Touati A., Telfer M. and Gullett B. (2000) Organohalogen Compd. 46, 264.
16. Gullett B., Altwicker E. and Touati A. (2000) Organohalogen Compd. 46, 102.
17. Blaha J. and Hagenmaier H. (1995) Organohalogen Compd. 23, 403.

Table 1. PCDD,F Formation Rates.

Ash	Mean PCDD,F Formation Rate, ng/g _{FA} Xs (mono- to octa-CDD,F) ∇ σ [No. samples] #note					
	N2	AIR	N2/Cl2	AIR/Cl2	CH4/Cl2	H2/Cl2
AR	154 ∇ 38 [2]	636 ∇ 319 [2]	3172 ∇ 233 [2]	3077 ∇ 1777 [3]	265 ∇ 92 [5]	342 ∇ 52 [2]
EX	42 ∇ 49 [2]	249 ∇ 83 [4]	2766 [1]	1747 ∇ 644 [2]	36 ∇ 21 [4] #1; 290 ∇ 71 [2] #2; 1448 ∇ 613 [2] #3	7 ∇ 6 [3] #4; 773 ∇ 418 [5] #5
OX	NM	36 ∇ 1 [2]	172 [1]	216 ∇ 215 [3]	77 ∇ 69 [18] #6; 1975 ∇ 324 [3] #7	189 ∇ 159 [4]

#1: $\phi_H \exists 1.39$; #2: 0.72 # ϕ_H #1.01; #3: $\phi_H = 0.5$.; #4: 0.1% O₂; #5, 14.5% O₂; #6: excludes 3 runs under #7; #7: 0.95 # ϕ_H , ϕ_V #1.02; NM = not measured.