

## Effects of solvent extractions on the thermal formation of PCDD/F on flyash samples enriched with $^{13}\text{C}$ -labelled amorphous carbon.

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### Abstract

Residues of thermally treated fly ash mixtures containing labelled amorphous carbon were analyzed for labelled and nonlabelled PCDD/F, where thermal treatments were applied prior to and after a series of solvent extractions on the flyash mixture. The formation of PCDD/F from pre-existing precursors present as adsorbates associated with the particulate carbon and fly ash was established, but the extent of this contribution to total PCDD/F formation remains unquantified. The results of this work indicates that the hypothesis of PCDD/F formation from particulate carbon must still be conclusively proven.

### Introduction

It is generally accepted that PCDD/F formation during municipal waste incineration is the result of catalytic reactions involving fly ash in the post-combustion zone. The nature and origin of precursors leading to these products continues to be a topic of extensive research. Historically, two basic approaches were taken in exploring fly ash mediated reactions; one being to examine PCDD/F formation from chemically obvious precursors such as chlorinated phenols, a proven reaction by use of labelled reagents<sup>1,2</sup>, while another approach is to examine PCDD/F formation from chemically dissimilar products, such as particulate carbon<sup>3,4</sup>.

In view of current opinion which suggests that potentially any source of carbon in the presence of chlorine and oxygen can ultimately lead to PCDD/F, and knowing that the highly adsorptive nature of carbon is exploited in many different applications, we felt that it was necessary to investigate the possibility of PCDD/F formation from adsorbates associated with the particulate carbon as a contributing factor to what has previously been hypothesised as *denovo* formation of PCDD/F from the particulate carbon itself.

Preliminary results presented by us in 1992, indicated that adsorbates on the particulate carbon could be a source of PCDD/F production in fly ash mediated reactions<sup>5</sup>. We now present additional data to support these findings.

### Experimental methods

#### Materials:

$^{13}\text{C}$ -Amorphous carbon (99% isotopic purity) was purchased from Aldrich,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  from J.T. Baker, deuterated chrysene from Cambridge Isotope Laboratories, and reagent grade KCl as well as all solvents (Onvisolv grade) from BDH. A standard solution containing all isomers of PCDD, PCDF and  $^{13}\text{C}$ -labelled PCDD of the tetra- to

octachlorinated congener groups was synthesized at the University of Waterloo<sup>6</sup>. Fly ash samples were obtained from an operating municipal waste incinerator in New York state.

*Fly ash pretreatment:*

Twenty grams of fly ash, homogenized and sieved to less than 180  $\mu\text{m}$  particle size was heated for at least 6 hours at 500  $^{\circ}\text{C}$  under an air flow of 50 mL/min to burn off all native carbonaceous species.

*Fly ash mixtures and reactions:*

A "carbon-free" mixture was prepared by addition of 1%  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 1% KCl to pretreated fly ash. The mixture was homogenized and divided into equal sized subsamples. A  $^{13}\text{C}$ -enriched mixture was prepared by adding 2%  $^{13}\text{C}$ -Amorphous carbon to one of the subsamples.

Samples of the carbon-free and  $^{13}\text{C}$ -enriched mixtures were thermally treated to establish background and initial PCDD/F formed under the reaction conditions. The remainder of the  $^{13}\text{C}$ -enriched mixture was Soxhlet extracted with toluene for 24 hours and dried under reduced pressure. Subsamples were removed for thermal treatment. The remainder of the mixture was further Soxhlet extracted with dichloromethane for 24 hours, dried under reduced pressure and subsamples were taken for thermal treatment.

*Thermal treatment of fly ash mixtures and analysis for PCDD/F formation:*

One to two grams of fly ash samples were packed in a glass column (280 mm x 8 mm i.d.), which was placed in a vertically oriented oven at 300  $^{\circ}\text{C}$  for 2 hours under an air flow rate of 50 mL/min. Exhaust gases were directed through an ice-cooled impinger containing toluene, to a fumehood via a florasil trap. The fly ash was transferred into a 25 mL screw-capped test tube and was extracted three times for 90 minutes by ultrasonication with 20 mL of toluene at 60  $^{\circ}\text{C}$ . The extracts and impinger contents were combined and reduced in volume to 100  $\mu\text{L}$  by rotary distillation and evaporation under nitrogen. Final extracts were analysed for PCDD/F using an HP 5890/5970 GC-MSD in SIM mode. Three characteristic ions were monitored for each congener group. A homemade 20 m column with liquid crystal stationary phase was used complimentary to a 30m DB-5 for confirmation of analysis<sup>7</sup>. Deuterated chrysene was used as a recovery standard.

## Results and Discussion

This set of experiments allowed us to examine the effects of carbon addition to fly ash on the background production of non labelled PCDD/F, as well as the effectiveness of solvent extractions on removing potential interfering compounds in the the production of PCDD/F in experiments pertaining to *denovo* formation from carbon. The results are shown in graphical form in Figures 1 and 2.

Common practices in exploring fly ash mediated reactions include thermal pretreatment of fly ash to burn off native PCDD/F and other carbonaceous species, often followed by "exhaustive" Soxhlet extraction, usually with toluene for 24 hours. Subsequent methods for removal of residual solvent vary. Control experiments are often performed to account for background production of PCDD/F.

The results presented in Figure 1 show a 20 fold increase in nonlabelled PCDD and 4 fold increase in nonlabelled PCDF production, effected by the addition of carbon to the mixture. Since the carbon is isotopically labelled, one can conclude that the increased production is most likely the result of the physical presence of carbon, rather than its chemical make-up. This trend was consistently observed in three other series of related experiments<sup>8</sup>. Thus, the commonly used method of determining "background" levels of PCDD/F production from pretreated fly ash samples is not always valid.

The results in Figure 2 show two very profound effects of solvent extraction on thermal PCDD production from carbon-enriched fly ash mixtures. Although only PCDD

results are indicated here, similar results were observed with PCDF. Based on papers presenting the *denovo* formation of PCDD/F from carbon, the expected products from this mixture were  $^{13}\text{C}$ -PCDD/F. While the PCDD production from the original nonextracted  $^{13}\text{C}$ -enriched mixture gave reasonable results from the standpoint of percentage labelled PCDD production to the total, which was 90% (the expected value based on isotopic purity of the carbon was 99%), after 24 hours of Soxhlet extraction with toluene, the relative production of labelled PCDD dramatically decreased to 40%, the consequence of nonlabelled PCDD production from residual solvent, as well as decreased production of labelled PCDD, which we believe to be the result of of toluene extractable adsorbates (precursors) that were removed from the carbon.

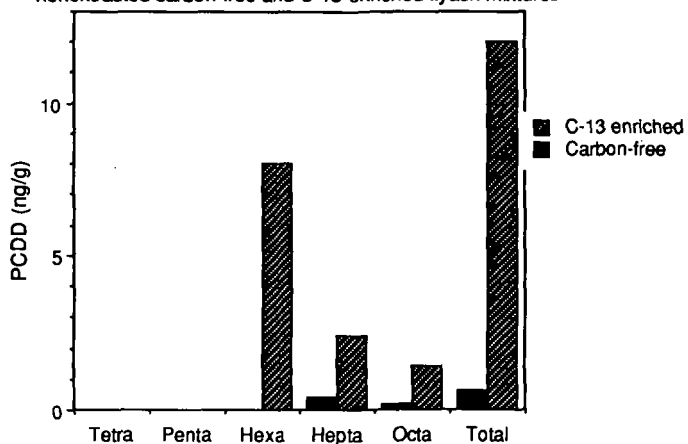
One very important implication of these results is that without the use of labelled carbon, a significant increase in PCDD production would have been observed and attributed to formation from carbon, when in fact 60% of the total was simply a consequence of "cleaning" the mixture.

After the second sequential extraction of the fly ash mixture using dichloromethane, the relative production of labelled PCDD increased to 70%. Overall, there was a significant decrease in the production of labelled PCDD after both solvent extractions, which we believe to be the result of an enhanced removal of extractable  $^{13}\text{C}$ -labelled organic precursors present as adsorbates on the particulate carbon. This observation raises important questions pertaining to experimental design often used in pursuing research on the *denovo* formation of PCDD/F from particulate carbon, as there is no obvious way of establishing with certainty that all adsorbates can be removed from particulate carbon. It is therefore our view that the widely accepted hypothesis of *denovo* formation of PCDD/F from particulate carbon on fly ash must still be conclusively proven.

## References

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Nonlabelled PCDD formed from thermal treatment of nonextracted carbon-free and C-13-enriched flyash mixtures



Nonlabelled PCDF formed from thermal treatment of nonextracted carbon-free and C-13-enriched fly ash mixtures

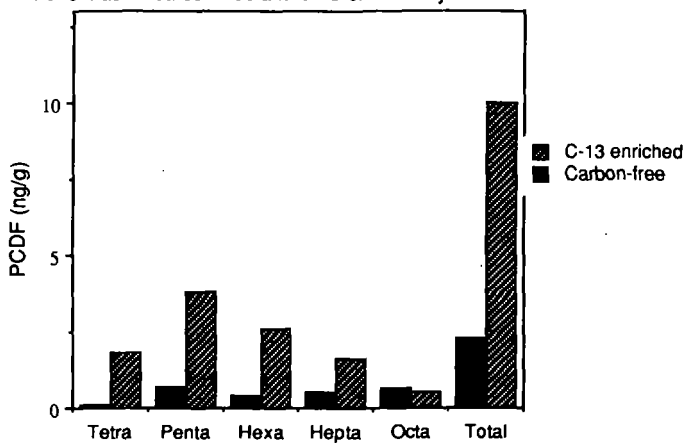


Figure 1: Nonlabelled PCDD and PCDF formed from nonextracted carbon-free and nonextracted <sup>13</sup>C-enriched fly ash mixtures.

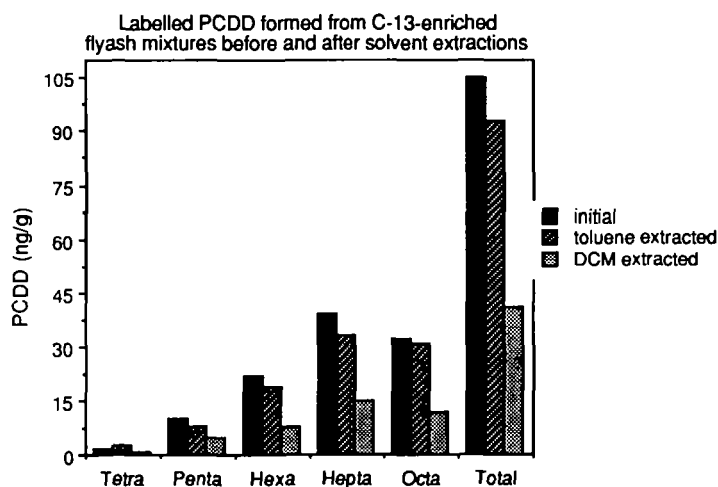
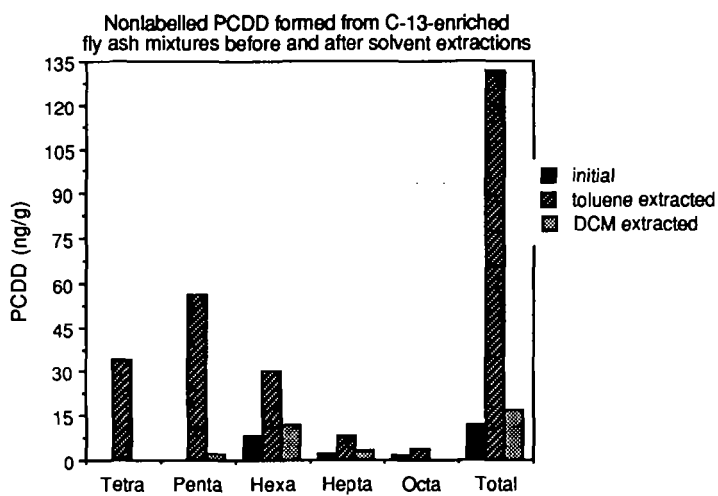


Figure 2: Nonlabelled and  $^{13}\text{C}$ -labelled PCDD formed from  $^{13}\text{C}$ -enriched flyash mixture before and after solvent extractions with toluene followed by dichloromethane.

