# THERMAL FORMATION OF DIOXINS AND DIOXIN-LIKE COMPOUNDS ON FLY ASH MATRIX FROM SECONDARY COPPER SMELTING PROCESSES

Liu GR, Wu JJ, Wang M, Jiang XX, Dong SJ, Zheng MH*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China
* Corresponding author, E-mail: zhengmh@rcees.ac.cn

## Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), and polychlorinated naphthalenes (PCNs) are persistent organic pollutants (POPs) that could be unintentionally formed during industrial thermal sources[1, 2]. Controlling and regulating the unintentional formation and emission of POPs from priority sources are the primary measures for protecting environment, and also with respect to sustainable development. Secondary copper smelting processes were considered as one of important sources of unintentional POPs including PCDDs, PCDFs and PCNs. Our previous studies investigated the emission levels and profiles of PCDDs, PCDFs and PCNs from several secondary copper smelting plants[3-6]. A large variation in concentrations of unintentional POPs was found for different case plants[3-6]. However, the key factors accounting for the formation levels of unintentional POPs have not been clarified.

Besides stack gas, fly ash was another important release route of unintentional POPs from industrial thermal sources[1]. Moreover, fly ash was considered as the important catalyzing matrix for formation of unintentional POPs during waste incinerations[7]. In our previous investigation, high contents of PCDDs, PCDFs and PCNs in fly ash samples collected from secondary copper smelting processes were observed[3, 6]. Thus, it was speculated that fly ash might play an important role in the formation of PCDDs, PCDFs and PCNs during secondary copper smelting processes. With regard to waste incineration, studies associated with the effect of fly ash on formation of unintentional POPs have been intensively carried out. For example, Cieplik et al. studied the formation of PCDD/PCDFs over fly ash from municipal solid waste incinerations (MSWI)[8], and confirmed that fly ash provided important carbon sources for the *de novo* synthesis of PCDD/PCDFs. Cains et al.[9] studied the effect of fly ash on PCDD/PCDF formation during waste incinerations, and compared the effect of fly ash with other carbon source on PCDD/PCDF formation. However, the effect of fly ash on PCDDs and PCDFs and PCNs has not been studied for secondary copper smelting. In this study, preliminary experiments were performed to investigate the effect of fly ash on formation of unintentional POPs during secondary copper smelting processes.

## Materials and methods

In this study, thermal reaction experiments with fly ash from a secondary copper smelter as matrix were performed in a laboratory tube furnace for the purpose of evaluating the effect of fly ash on the thermal formation of PCDDs, PCDFs and PCNs. The fly ash was collected from a plant with 100% of copper scrap as raw materials. In this smelter, a reverberatory furnace was used for the secondary copper smelting. The production capacity of the smelter was 110 tons per furnace. A large amount of air was introduced into the dust arrestor during cooling stage of smelting process. Therefore, air was adopted to pass through the laboratory furnace during the thermal reaction experiments. In the preliminary study, a relatively low temperature of 250 °C was set with a reaction time of 30 minutes. The residue ash and produced gas absorbed by XAD-2 resin were combined and analyzed for PCDDs, PCDFs and PCNs. Analysis of PCDDs, PCDFs and PCNs were performed by isotopic dilution high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS) techniques. The detail description on the sample extraction, preparation and instrumental analysis has been reported in US EPA 8290 and our previous publications[10].

**Results and discussion**

In this preliminary study, the toxic equivalent (TEQ) changes of PCDDs, PCDFs and PCNs before and after the thermal treatment were focused. The PCN TEQ was calculated according to the toxic equivalent factors (TEF) summarized by Noma et al.[11]. The TEQ changes from tetra- to octa- homologs of PCDDs, PCDFs and PCNs were presented in Fig 1. For PCDF homologs, the most obvious increase of TEQ was observed for OCDF and followed by heptaCDF. The TEQ changes are not very obvious for lower chlorinated homologs of PCDFs. Very similar trend was also found for homologs of PCDDs. TEQ change in OCDD were the most significant followed by heptaCDD. For lower chlorinated homologs of PCDDs, the increase of TEQ was not obvious and an even decrease of TEQ in tetraCDD was found. As regards PCNs, the significant increases in TEQ were observed for hexa- and hepta- homologs. The TEQ increment in pentaCN was the lowest with a value of lower than 2.

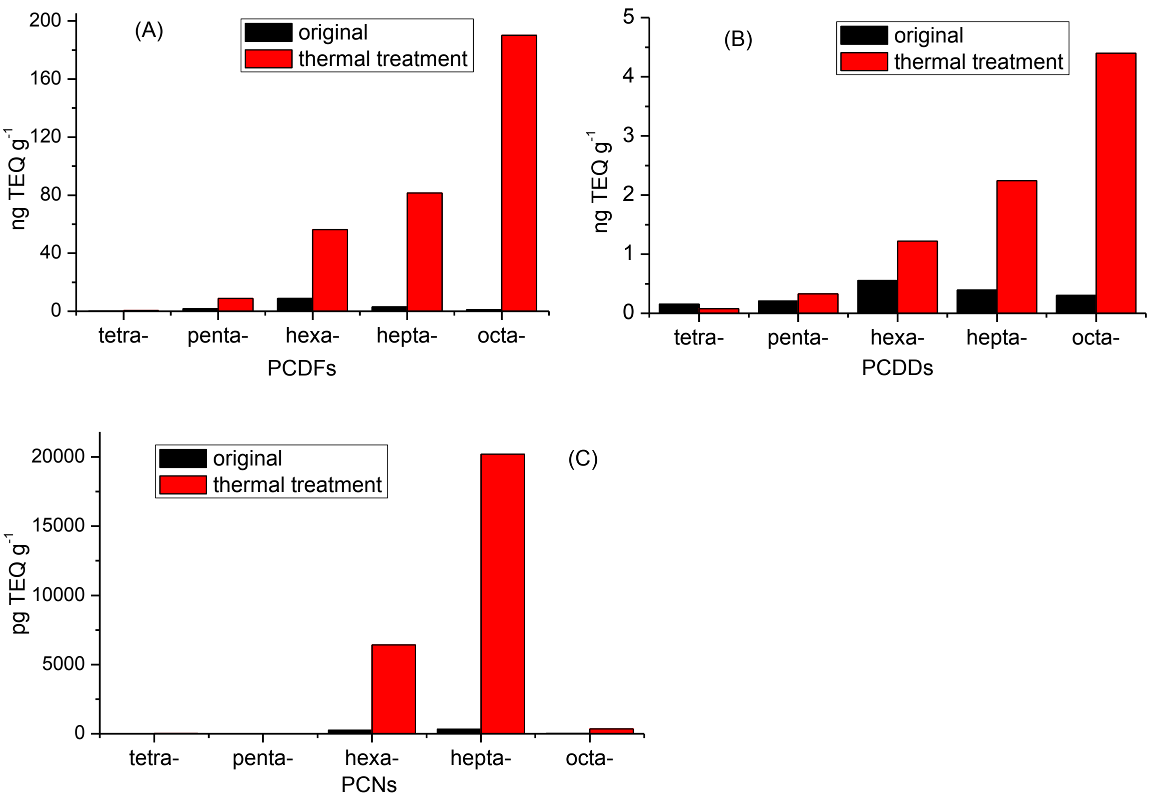


Fig. 1 TEQ increments of PCDFs, PCDDs, and PCNs after thermal treatment of fly ash in tube furnace

Contents of several important elements including copper, zinc and chlorine in fly ash are widely recognized as important for catalyzing formation of unintentional POPs[12-14]. In this study, the contents of copper and zinc in fly ash were determined by inductively coupled plasma-optical emission spectrometry, and the values were 260 and 166 mg $g^{-1}$ respectively. The fraction of chlorine in fly ash is about 6.9% by X-ray fluorescence. Those values indicated relative high contents of copper, zinc and chlorine in fly ash. It was therefore speculated that high copper, zinc and chlorine contents in the fly ash might be one of important factors contributing to significant formations of unintentional POPs. Further studies with the aim of clarifying the key factors and possible mechanism of unintentional POPs during secondary copper smelting processes are still in process.

Generally, the elevated levels of PCDD, PCDF and PCN TEQs after thermal reactions were about several hundred times higher than the levels in original fly ash, which indicating significant promoting effect of fly ash on formation of unintentional POPs during secondary copper smelting process. The fly ash was normally recycled into raw materials for some secondary copper smelting plants. The results in this preliminary study suggested fly ash should not be simply recycled into raw materials for secondary copper smelting.

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