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Comparison of PCDD/F levels and profiles in fly ash samples from multiple industrial thermal sources

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HIGHLIGHTS

- PCDD/F profiles in fly ash from 14 industrial sources were presented and compared.
- PCDD/F levels were highest in fly ash samples from secondary copper smelting.
- Source-specific ratios of PCDD/F congeners were suggested as diagnostic values.
- Equations describing correlations between congeners and PCDD/F TEQs were developed.

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ABSTRACT

A comprehensive comparison of the levels and profiles of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in fly ash samples from multiple industrial sources may help to prioritize sources and to understand discrepancies in profiles. In this study, PCDD/F data from 113 fly ash samples from 14 sources reported in previous studies were summarized and compared. The highest PCDD/F levels occurred in samples from secondary copper smelting (SCu). Although PCDD/F levels from secondary zinc smelting (SZn) were slightly lower than those of SCu, the PCDD/F profiles varied widely between the two sources. For SCu, more chlorinated homologs were dominant, with highest degrees of chlorination being 6.6 for PCDF and 7.2 for PCDD. For SZn, less chlorinated homologs were dominant, with lowest degrees of chlorination being 4.4 for PCDF and 4.8 for PCDD. We speculate that copper and zinc might promote PCDD/F formation by catalyzing different pathways of thermal reactions. Diagnostic ratios of specific PCDD/F congeners for different sources were suggested to identify potential sources of PCDD/Fs in the environment. Equations describing correlations between congeners and PCDD/F toxic equivalents were established, which may be useful for rapid and inexpensive screening of the toxic levels of PCDD/Fs in fly ash samples.

1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) pose potential risks to environmental and human health globally because of their toxicity, persistence, and long-range transport. Unintentional formation and emission from various industrial activities are the major sources of PCDD/Fs (Fiedler et al., 2000; Weber et al., 2008; Holt et al., 2010). Among industrial sources, waste incineration and metal smelting processes are widely recognized as the main sources of the formation and emission of PCDD/Fs (Gullett et al., 2000; Aries et al., 2006; Ni et al., 2009; Ba et al., 2009b).

Solid residue and stack gas emissions are considered to be the most important release pathways of PCDD/Fs and other dioxin-like compounds from waste incineration and metal smelting processes (Fiedler, 2007; Liu et al., 2009, 2010, 2012, 2013, 2014). Heterogeneous reactions during thermal processes are the dominant formation mechanisms of PCDD/Fs (Takasuga et al., 2000). It is widely recognized that fly ash (a solid residue) can promote PCDD/F formation by heterogeneous reactions during industrial thermal processes, as a result of the abundant carbonous residue and catalytic elements contained in fly ash (Tuppurainen et al., 2003; Chen et al., 2008; Altarawneh et al., 2009; Cobo et al., 2009). For stack gas emissions, air pollution control devices are normally installed in industrial plants for the purpose of removing contaminants from stack gas prior to emission to the atmosphere. Thus, reductions in emissions of dioxins might be achieved by the

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physical removal of fly ash particles containing PCDD/Fs (Chi et al., 2008). For example, although reductions in PCDD/F atmospheric emissions have been achieved through the removal of fly ash particles by dual bag filters (Chi et al., 2008), PCDD/Fs produced were actually not destroyed; this means that most of the produced PCDD/Fs were transferred into solid residues, including fly ash, by air pollution control devices. The treatment of solid residues containing PCDD/Fs remains a problem. Therefore, stack gas emissions of dioxins might accurately represent emissions into ambient air, while not accurately reflecting the formation levels and patterns of PCDD/Fs during industrial thermal processes. The PCDD/F levels and profiles of fly ash might be more representative than those of stack gas for studying the unintentional formation patterns of PCDD/Fs and underlying mechanisms.

A comprehensive and systematic evaluation and comparison of the PCDD/F levels and profiles from multiple industrial thermal sources may be helpful in prioritizing the sources, understanding their discrepancies in profiles, and identifying potential indicators of PCDD/F toxic equivalents (TEQs) (Fiedler et al., 2000; Grochowalski et al., 2007). Among numerous industrial thermal sources, waste incineration and metal smelting processes have been the main focus of PCDD/F emission studies (Yu et al., 2006; Gao et al., 2009; Ni et al., 2009; Ba et al., 2009b). Fiedler et al. (2000) evaluated PCDD/F patterns by statistically analyzing 109 stack gas samples from municipal solid waste incinerators, hazardous waste incinerators, and the iron and steel industries. Potential TEQ indicators of atmospheric PCDD/F emissions have also been identified by the statistical analysis of stack gas emissions samples (Fiedler et al., 2000; Gullett and Wikström, 2000; Oh et al., 2004; Jansson and Andersson, 2012). Fly ash, a solid residue, is an important pathway for the release of PCDD/F and is the most important catalytic matrix for the promotion of PCDD/F formation by heterogeneous reactions. However, a comprehensive and systematic evaluation and comparison of the PCDD/F levels and profiles of fly ash samples from multiple industrial thermal processes is still lacking.

Previous studies have reported on PCDD/F concentrations and profiles of fly ash samples from coking processes (Liu et al., 2013), primary magnesium smelting processes (Nie et al., 2011), primary copper smelting processes, (Nie et al., 2012a) and secondary copper, aluminum, zinc, and lead smelting processes (Ba et al., 2009a,b; Nie et al., 2012b), and iron and steel making (Lv et al., 2011a,b). In this study, data from studies on the PCDD/F levels and profiles of fly ash were summarized and compared (Ba et al., 2009a,b; Nie et al., 2011, 2012a,b; Lv et al., 2011a,b, 2013); and PCDD/F data from 113 fly ash samples from 14 types of industrial thermal sources were systematically evaluated and compared. To the best of our knowledge, this is the most comprehensive and systematic analysis of PCDD/F levels and profiles in fly ash sample from multiple industrial thermal sources in China. The primary aims of this study were: (1) to compare the formation levels of PCDD/Fs from multiple industrial sources, which could help understand the priority sources of PCDD/F formation, and to implement control activities for inhibiting PCDD/F formation; (2) to obtain a comprehensive evaluation of the differences in homolog distributions and congener profiles of PCDD/Fs from multiple industrial thermal sources, which might enhance the understanding of PCDD/F patterns and potential mechanisms involved; (3) to assess the correlations between specific congeners and PCDD/F TEQs in the solid residue phase, which could help identify the potential marker congeners of PCDD/F formation in solid residues that occur industrial thermal processes.

2. Materials and methods

2.1. Information on the fly ash samples

We have previously reported on several studies of dioxin concentrations, profiles, and emission factors in fly ash samples from coking processes (Liu et al., 2013), primary magnesium smelting (Nie et al., 2011), primary copper smelting processes (Nie et al., 2012a) and secondary copper, aluminum, zinc and lead smelting processes (Ba et al., 2009a,b; Nie et al., 2012b), and iron and steel making (Ba et al., 2009a,b; Lv et al., 2011a,b). In those studies, fly ash samples produced during different incineration or metal smelting stages were collected from the dust arrestors (bag fabric filters, electrostatic precipitator, and cyclones). In this study, the PCDD/F levels and profiles in fly ash samples from municipal solid waste incineration, hazardous waste incineration, iron ore sintering, and converter steel-making were determined. Data on the PCDD/F levels and profiles in fly ash from previous studies were also summarized and included for comparison. PCDD/F data from 113 fly ash samples obtained from 14 types of industrial thermal source in China were collected and evaluated. Basic information on the source categories and fly ash samples is presented in Table 1.

2.2. Chemical analysis, quality assurance, and quality control

PCDD/Fs were analyzed by isotope dilution high resolution gas chromatography-high resolution mass spectrometry (HRGC/HRMS) according to US Environmental Protection Agency (EPA) method 8290. Details of the sample extraction, cleanup, and instrumental analysis procedures for the PCDD/Fs have been described in detail in our previous studies (Ba et al., 2009b; Liu et al., 2013). Briefly, the fly ash samples were spiked with known amounts of $^{13}C_{12}$-labeled PCDD/Fs, treated with 1 mol L^{-1} HCl, then Soxhlet

Table 1
Basic information on the source categories and fly ash samples.

Source category	Abbreviation	APCD	Number of samples	Ref.
Municipal solid waste incineration	MSWI	Bag filter	14	–
Hazardous waste incineration	HWI	Bag filter	11	–
Thermal wire reclamation	TWR	Bag filter	3	(Nie et al., 2012b)
Converter furnace for steel-making	CVF	Bag filter	4	–
Iron ore sintering	IOS	Electrostatic precipitator or cyclones	4	–
Iron foundry	IC	Bag filter	14	(Lv et al., 2011a)
Coking processes	CP	Bag filter	16	(Liu et al., 2013)
Secondary copper smelting	SCu	Bag filter	14	(Ba et al., 2009b; Nie et al., 2012a)
Secondary aluminum smelting	SAl	Bag filter	13	(Ba et al., 2009b)
Secondary zinc smelting	SZn	Bag filter	2	(Ba et al., 2009a)
Secondary lead smelting	SPb	Bag filter	2	(Ba et al., 2009a)
Primary copper smelting	PCu	Bag filter	2	(Nie et al., 2012a)
Primary magnesium smelting	PMg	Bag filter	5	(Nie et al., 2011)
Hot dip galvanizing	HDG	Diffuse ash	9	(Lv et al., 2011b)