



Emissions of 2,3,7,8-substituted and non-2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans from secondary aluminum smelters

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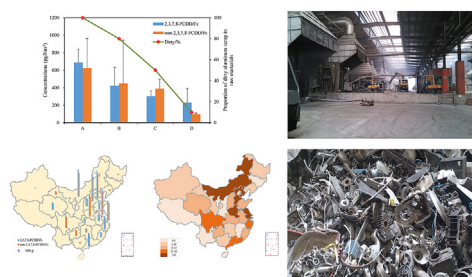
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HIGHLIGHTS

- Emission of 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs was investigated.
- The impacts of raw material composition on PCDD/F levels and profiles were studied.
- Non-2,3,7,8-PCDD/Fs can be transformed into 2,3,7,8-PCDD/Fs, elevating risks.
- PCDD/F concentrations increased as the content of dirty aluminum scrap increased.

GRAPHICAL ABSTRACT



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ABSTRACT

The secondary aluminum smelting industry is an important source of polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs). However, the formations and emissions of non-2,3,7,8-PCDD/Fs have rarely been studied. Non-2,3,7,8-PCDD/Fs may also be metabolically toxic to mammals. In this study, four typical secondary aluminum smelters were selected as demonstration smelters and the composition of the raw material they used was adjusted to investigate the influence on PCDD/F emissions and profiles. In addition to 17 congeners of 2,3,7,8-PCDD/Fs, 64 congeners of non-2,3,7,8-PCDD/Fs were firstly reported. Strong, positive correlations were found between non-2,3,7,8-PCDD/Fs and 2,3,7,8-PCDD/Fs. The concentrations of 2,3,7,8-PCDD/Fs in stack gas and fly ash samples were 120.7–870.4 pg/Nm³ and 13.40–292.9 ng/g, respectively. Those of non-2,3,7,8-PCDD/Fs in the stack gas and fly ash samples were 84.03–1183.7 pg/Nm³ and 7.20–344.7 ng/g, respectively. The raw material composition was a key factor affecting PCDD/F emissions and profiles. An analysis of Gibbs free energies (ΔG_f) showed that non-2,3,7,8-PCDD/Fs could be transformed into 2,3,7,8-PCDD/Fs, which would increase the PCDD/F environmental risks. The emission inventories of 2,3,7,8-PCDD/Fs, non-2,3,7,8-PCDD/Fs, and International Toxic Equivalents from Chinese secondary aluminum smelters in 2013 were 8247 g, 7253 g, and 608.6 g, respectively. The results of this study could contribute to potential risk evaluations and effective reduction of non-2,3,7,8-PCDD/Fs.

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1. Introduction

Aluminum can be produced from bauxite ore or recovered by recycling aluminum scrap. During the secondary production process from scrap, aluminum is melted in a furnace, and impurities are typically removed using chlorine until the aluminum reaches the desired purity (Tondeur et al., 2015). The presence and incomplete combustion of organic impurities on the scrap may lead to unintentional formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Ba et al., 2009; Shao et al., 2010; Hu et al., 2013a; Subedi et al., 2014; Wang et al., 2016a; Su et al., 2017). Organic impurities on scrap or other sources of carbon can generate PCDD/Fs when reacting with inorganic chlorides or organically bound chlorine at 250–450 °C (Ba et al., 2009). Additionally, PCDD/F synthesis can occur when the stack gas (SG) is cooled through the re-formation window (Eduljee and Dyke, 1996).

Secondary aluminum smelting industry is widely recognized as an important source of PCDD/Fs in the Stockholm Convention. Ba et al. (2009) measured PCDD/F emissions from Chinese secondary aluminum smelters and reported an International Toxic Equivalent (I-TEQ) range of 0.053–0.72 ng TEQ/Nm³. Comparable levels of PCDD/Fs were found at secondary aluminum smelters in Poland by Grochowalski et al. (2007), and the total TEQs (0.03–0.58 ng TEQ/Nm³) were much higher than those for other industrial thermal processes. Although some studies have investigated PCDD/F emissions during secondary aluminum smelting processes, these studies have focused only on toxic 2,3,7,8-PCDD/Fs and total homologue groups. Such results did not reveal the subtle details that can be derived from the study of individual congeners. Besides, the formations, concentrations, and profiles of non-2,3,7,8-PCDD/Fs during secondary aluminum smelting processes have rarely been reported.

Some toxicology and metabolism studies on non-2,3,7,8-PCDD/F congeners have confirmed their potential toxicity. For instance, the effects of 1,2,3,4-TCDD on drug-metabolizing enzymes were studied in male and female rats (Hanioka et al., 1994). This research showed that 1,2,3,4-TCDD induced the CYP1A subfamily P450 in male and female rats, and that 1,2,3,4-TCDD was a bifunctional inducer of drug-metabolizing enzymes. Unexpectedly, the researchers also found that 1,2,3,4-TCDD may have some 2,3,7,8-TCDD-like toxicity. To gain a better understanding of the mammalian metabolism of PCDD/Fs, 1,2,7,8-TCDD was utilized to conduct a tissue distribution, excretion, and metabolism study (Hakk et al., 2001). The study data showed that 1,2,7,8-TCDD had significant potential to interfere with thyroid hormone homeostasis via hydroxylation to the TTR-competitive binding species, 2-OH-1,3,7,8-TCDD. Conceivably, non-2,3,7,8-PCDD/F congeners may also be metabolically toxic to mammals.

For comprehensive monitoring of PCDD/F emissions and control of the potential risks, careful examination of emissions and profiles of both 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs offers definite advantages over measurement of only the 2,3,7,8-PCDD/Fs. Previous studies have evaluated different gas chromatography (GC) columns for separation of all 136 tetra- to octa-chlorinated PCDD/Fs from closely eluting congeners (Fishman et al., 2011; Do et al., 2013), and identified their retention times and elution orders. These results could be applied to a comprehensive study of 2,3,7,8-PCDD/F and non-2,3,7,8-PCDD/F emissions. It is therefore important to obtain a full picture (however approximate) of tetra- to octa-chlorinated PCDD/Fs and to explore the transformation pathways and deduce the chemical behavior of different PCDD/F congeners during secondary aluminum smelting processes. The results of this study could contribute to risk evaluations and control of PCDD/F emissions from secondary aluminum smelters globally, and will be beneficial for the protection of human and environmental health.

2. Material and methods

2.1. Demonstration smelters and sample collection

Four typical secondary aluminum smelters (labeled A, B, C, and D) located in Shandong and Hebei provinces in China were selected as demonstration smelters to investigate the formations and emissions of 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs. Previous studies have indicated that the raw material, smelting technique, and furnace capacity might influence the emissions of unintentionally produced persistent organic pollutants during industrial thermal processes (Li et al., 2007; Ba et al., 2009; Wang et al., 2010; Hu et al., 2014). The capacities of the smelters ranged from 11,000 to 120,000 tons per year. All of the smelters were equipped with reverberatory furnaces and bag filter air pollution control systems, which are used by most of the secondary aluminum smelters globally. The proportions of dirty aluminum scrap (used and discarded material with high content of organic impurities, such as appliances, aluminum foil, automobile and airplane parts, aluminum sidings, and beverage cans) and clean aluminum scrap (pre-consumer scrap material, such as waste from the drilling and machining of aluminum castings, waste from fabrication and manufacturing operations, and dross skimmed off molten aluminum during the smelting process) in the raw material could be easily adjusted and may play a key role in the PCDD/F emissions. Therefore, we adjusted the composition of the raw material with dirty aluminum scrap of 100%, 80%, 50%, and 10% in smelters A, B, C and D, respectively, to evaluate how the raw material composition affected the PCDD/F emissions and profiles. Detailed information for smelters A, B, C, and D is shown in Table S1 of the Supporting Information.

Three or four SG samples and one fly ash (FA) sample were collected from each smelter. The SG samples were collected using an automatic isokinetic sampling system (Isostack Basic; Tecora Corp., Milan, Italy) that has been widely used in previous studies (Liu et al., 2013; Wang et al., 2016b) following the European Union standard method EN-1948. The sampling system consisted of a heated titanium probe, a filter box with a Whatman quartz microfibre thimble filter (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA), and a water-cooled Amberlite XAD-2 adsorbent trap (Supelco, Bellefonte, PA, USA). A ¹³C-labeled standard (EN-1948 SS; Cambridge Isotope Laboratories, Andover, MA, USA) was added as a sampling standard before sampling to evaluate the sampling efficiency. After sampling, the samples were wrapped tightly in aluminum foil and packed in sealed polyethylene bags to prevent sample contamination and target loss. The FA samples were collected from the bag filter outlet during SG sampling.

2.2. PCDD/F analysis

Pretreatment and analysis of the SG and FA samples for PCDD/Fs followed the standard methods EN-1948 and US EPA-1613, which have been described in detail previously (Ba et al., 2009; Nie et al., 2012; Hu et al., 2013b; Han et al., 2016; Wang et al., 2016b). Briefly, each sample was spiked with 1 ng of a ¹³C-labeled PCDD/F internal standard mixture (EN-1948 ES, Cambridge Isotope Laboratories; EPA-1613 LCS, Wellington Laboratories, Guelph, Canada) and then Soxhlet-extracted with 250 mL of toluene for approximately 24 h. Before extraction, the FA samples were treated with 1 M HCl. Each extract was purified using an acidic silica gel column, a multilayer silica gel column, and then a basic alumina column. To quantify the native PCDD/Fs and labeled internal standards, the final extract was concentrated to 20 µL and spiked with 1 ng of a ¹³C-labeled injection standard (EN-1948 IS, Cambridge Isotope Laboratories; EPA-1613 IS, Wellington Laboratories) before instrumental analysis.

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