Science of the Total Environment 649 (2019) 473–481

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Emission profiles and formation pathways of 2,3,7,8-substituted and non-2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans in secondary copper smelters

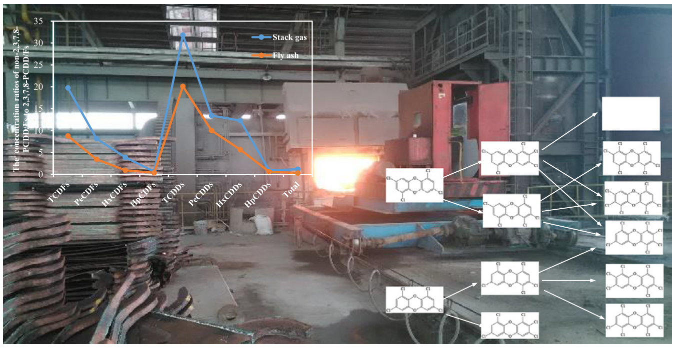
Haifeng Li [a,b], Wenbin Liu [a,b,*], Chen Tang [a], Rongrong Lei [a,b], Wen Zhu [a]

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, No.18, Shuangqing Road, Beijing 100085, China*
[b] *University of Chinese Academy of Sciences, No.19A, Yuquan Road, Beijing 100049, China*

HIGHLIGHTS

- A full picture of 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs were investigated.
- Non-2,3,7,8-PCDD/Fs are essential for grasping the PCDD/F formation mechanisms.
- PCDD/F emissions via solid residues were obviously higher than gaseous matter.
- Chlorination is crucial for conversion among 2,3,7,8-PCDDs and non-2,3,7,8-PCDDs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 July 2018
Received in revised form 15 August 2018
Accepted 21 August 2018
Available online 25 August 2018

Editor: Jay Gan

Keywords:
Non-2,3,7,8-PCDD/Fs
Secondary copper smelting
Emission factors
Transformation pathway

ABSTRACT

Secondary copper smelting production is one of the largest polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) emission sources in the world. However, the formations and emissions of non-2,3,7,8-PCDD/Fs have rarely been studied. Toxicology and metabolism studies have proved that non-2,3,7,8-PCDD/Fs may also be toxic to mammals. To better explore the pathways and mechanisms involved in transformation among non-2,3,7,8-PCDD/F and 2,3,7,8-PCDD/F congeners, their full picture was investigated in stack gas and fly ash samples collected in typical secondary copper smelting plants. The concentration ranges for 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs in the stack gas samples were 0.09–5.24 ng/Nm^3 and 0.11–7.47 ng/Nm^3, respectively. The corresponding concentration ranges in the fly ash samples were 20–2712 ng/g and 2.7–818 ng/g. PCDD/F emissions were mainly from the oxidation stage, and these emissions contributed to 42.6–44.8% of the total emissions from the secondary copper smelting processes. Lower chlorinated PCDD/Fs partitioned more into the stack gas, whereas higher chlorinated PCDD/Fs were more likely to concentrate in the fly ash. Non-2,3,7,8-PCDD/Fs were more likely than 2,3,7,8-PCDD/Fs to associate with the gas phase. Chlorination transformation may occur among PCDD congeners, including 2,3,7,8-PCDD and non-2,3,7,8-PCDD congeners.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), listed in the Stockholm Convention Annex C, have become a global environmental hot issue because of their high toxicity, persistence, long-

---

* Corresponding author at: State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Beijing 100085, China.
E-mail address: liuwb@rcees.ac.cn (W. Liu).

https://doi.org/10.1016/j.scitotenv.2018.08.279

range transport, and bioaccumulation (Chen et al., 2018; Han et al., 2015; Nie et al., 2012a; Wania and Mackay, 1996). PCDD/Fs can be unintentionally produced by many industrial and agricultural processes, such as waste incineration, iron ore sintering, secondary metal production, and heat and power generation (Du et al., 2010; UNEP, 2013; Xu et al., 2009). Secondary copper smelting production is one of the largest PCDD/Fs emission sources in China, releasing 962.5 g toxic equivalent quantity (TEQ) PCDD/Fs to the environment in 2013, and accounting for approximately 10% of the total releases from all types of sources according to the National Implementation Plan of China.

Secondary copper is obtained from copper scrap or other copper-containing sources such as electronic scrap, sludge, and dross from refineries (UNEP, 2013). PCDD/Fs probably form because of the presence of trace oils, plastics, and other organic materials in feeds and fuels. Organic materials can produce carbon particles that react with inorganic chlorides or organically bound chlorine at 200–500 °C (UNEP, 2007; Zou et al., 2012). This formation process is catalyzed by the presence of metals, especially highly potent copper catalysts (Nganai et al., 2011). Synthesis of PCDD/Fs can also take place as the stack gas is cooled through a “reformation window”, which can be present in abatement systems and the furnace cooler (Eduljee and Dyke, 1996; UNEP, 2007). Secondary copper smelting process typically has three main smelting stages: feeding-fusion (FF), oxidation (OX), and deoxidization (DO). During each smelting stage, the formation and emission of PCDD/Fs may occur because of incomplete combustion of organic impurities in the raw material, fuel, or reductant (e.g., coal). Furthermore, PCDD/F emissions and profiles at different smelting stages may differ because of differences in the operating conditions and feed materials used in these stages.

Issues associated with the formations, emissions, profiles, and environmental risks of tetra- to octa-CDD/Fs during secondary copper smelting processes have been investigated over the past decade (Ba et al., 2010; Hu et al., 2014; Nie et al., 2012a). Large variations in PCDD/F concentrations have been observed. High concentrations of PCDD/Fs (0.043–15.8 ng TEQ/Nm^3) were measured in Chinese secondary copper smelters (Ba et al., 2009a). Relatively low levels of PCDD/Fs were detected in Poland (0.002–1.27 ng TEQ/Nm^3) (Grochowalski et al., 2007) and Taiwan (<0.15 ng TEQ/Nm^3) (Hung et al., 2015). However, the formations and emissions of non-2,3,7,8-PCDD/Fs have rarely been studied in previous studies, which also play an important role in understanding the formation mechanisms of PCDD/Fs. Yang et al. (2017) clarified the reaction pathways for thermochemical formation of PCDDs from 2,3,6-trichlorophenol by detecting free radical intermediates and non-2,3,7,8-PCDD/F congeners. Toxicology and metabolism studies have shown that non-2,3,7,8-PCDD/F congeners may also be toxic to mammals (Hakk et al., 2001; Hanioka et al., 1994; Petroske et al., 1997).

Therefore, it is essential to obtain a full picture of tetra- to octa-CDD/Fs and to better explore their formation mechanisms in secondary copper smelting processes. In this study, the emissions and profiles of 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs were investigated in typical secondary copper smelters. The results will improve our understanding of PCDD/F formations and emissions, and provide some clues about the pathways and mechanisms involved in transformation between non-2,3,7,8-PCDD/F and 2,3,7,8-PCDD/F congeners.

2. Material and methods

2.1. Sampling

Three typical secondary copper smelting plants in China (labeled DC, DY, and LY) were selected and characterized for the emissions, profiles, and transformation pathways of PCDD/Fs. Plants DC and DY were equipped with reverberator furnaces, which are widely used in China for secondary copper smelting. Plant LY used a NGL (Nanchang Gutiyelian Lu) furnace, which combines a titling furnace and rotary furnace. Scrap copper, blister copper, and anode copper were used as raw materials in the three investigated plants. All the feed materials used in the sample plants were pre-cleaned by sorting, washing, depitching, crushing, and drying. Fabric bag filters were used for air pollution control in all of the plants, and their capacities ranged from 35,000–150,000 t/year. Details for the investigated plants are given in Table S1.

Stack gas samples were collected during the three smelting stages using an automatic isokinetic sampling system (Isostack Basic; Tecora Corp., Milan, Italy) following standard method EN-1948 (Hu et al., 2013b). Details on smelting processes and smelting conditions of different smelting stages are given in Table S2. The sampling system contained a heated titanium probe, a filter box equipped with a quartz-fiber thimble filter, and a water–cooled XAD–2 adsorbent trap (Supelco, Bellefonte, PA, USA). The resin was spiked with a $^{13}C_{12}$-labeled standard (EN-1948 SS; Cambridge Isotope Laboratories, Andover, MA, USA) before sampling to evaluate the sampling efficiency. After collection, all samples were tightly wrapped in aluminum foil and packed in sealed polyethylene bags to prevent contamination and loss. The samples were then transferred to the laboratory and stored at −18 °C until required for analysis. Fly ash samples were collected from the bag filter outlet during stack gas sampling.

2.2. Sample preparation and analysis

The pretreatment and analysis of the stack gas and fly ash samples for tetra- to octa-CDD/Fs were performed in accordance with standard methods EN-1948 and US EPA-1613, which have been described in previous studies (Ba et al., 2010; Holt et al., 2012; Huang et al., 2014; Nie et al., 2012b; Wang et al., 2012). Briefly, the samples were spiked with 1 ng of $^{13}C_{12}$-PCDD/F internal standards (EN-1948 ES, Cambridge Isotope Laboratories; EPA-1613 LCS, Wellington Laboratories, Guelph, Canada), and then Soxhlet extracted with 250 mL of toluene for about 24 h. The fly ash samples were pretreated with 1 M HCl before extraction. The extracts were concentrated to about 1–2 mL using a rotary evaporator, and then successively cleaned using acidic silica gel, multi-layer silica gel, and alumina columns. Finally, the extracts were concentrated to about 20 μL using a rotary evaporator and under a gentle stream of nitrogen. Before instrumental analysis, each extract was spiked with 1 ng of $^{13}C_{12}$-PCDD/F injection standards (EN-1948 IS, Cambridge Isotope Laboratories; EPA-1613 IS, Wellington Laboratories) to calculate the recoveries.

The PCDD/Fs were analyzed with an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA) coupled with a Autospec Ultima high-resolution mass spectrometer (MS) (Waters, Milford, MA). A DB-5 MS fused-silica column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies) was used for separation of the congeners. The mass range of the MS was calibrated using perfluorokerosene, and the MS was operated in selected ion monitoring mode with a resolution >10,000. The MS was equipped with a positive electron ionization source and the electron energy was 38 eV.

The PCDD/F congeners and total homologues were identified and quantified based on their retention times and isotope ratios (Wang et al., 2016). In this study, all tetra- to octa- CDD/Fs in the stack gas and fly ash samples were fully analyzed. Some 2,3,7,8-PCDD/F congeners were contained in the $^{13}C_{12}$-PCDD/F internal standards, and these congeners were identified and quantified using the corresponding internal standards. The congeners without $^{13}C_{12}$-labeled internal standards were identified and quantified using the closest eluting stable isotope labeled internal standard. Blank experiments were carried out in each batch of samples for quality control. The recoveries for the $^{13}C_{12}$-labeled 2,3,7,8-PCDD/Fs were 60–145% and 41–117% in the stack gas and fly ash samples, respectively.