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Polychlorinated dibenzo-*p*-dioxin and dibenzofuran and polychlorinated biphenyl emissions from different smelting stages in secondary copper metallurgy

Jicheng Hu, Minghui Zheng *, Zhiqiang Nie, Wenbin Liu, Guorui Liu, Bing Zhang, Ke Xiao

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

HIGHLIGHTS

- ▶ Dioxin emissions from different secondary copper smelting stages were investigated.
- ▶ Feeding-fusion was identified as main dioxin emission stage during smelting.
- ▶ Raw material composition significantly influenced PCDD/F and PCB discharges.

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ABSTRACT

Secondary copper production has received much attention for its high emissions of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) reported in previous studies. These studies focused on the estimation of total PCDD/F and polychlorinated biphenyl (PCB) emissions from secondary copper smelters. However, large variations in PCDD/F and PCB emissions reported in these studies were not analyzed and discussed further. In this study, stack gas samples at different smelting stages (feeding-fusion, oxidation and deoxidization) were collected from four plants to investigate variations in PCDD/F and PCB emissions and characteristics during the secondary copper smelting process. The results indicate that PCDD/F emissions occur mainly at the feeding-fusion stage and these emissions contribute to 54–88% of the total emissions from the secondary copper smelting process. The variation in feed material and operating conditions at different smelting stages leads to the variation in PCDD/F emissions during the secondary copper smelting process. The total PCDD/F and PCB discharge (stack gas emission + fly ash discharge) is consistent with the copper scrap content in the raw material in the secondary copper smelters investigated. On a production basis of 1 ton copper, the total PCDD/F and dl-PCB discharge was 102, 24.8 and 5.88 μg TEQ t^{-1} for the three plants that contained 100%, 30% and 0% copper scrap in their raw material feed, respectively.

1. Introduction

Relevant studies have indicated that polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) emissions from secondary copper smelters are higher than those from iron foundries, secondary aluminum smelters and even waste incinerators (Chien-Min, 2004; Yu et al., 2006; Ba et al., 2009; Lv et al., 2011). Secondary copper production is becoming increasingly important owing to the increased demand for copper metal and decreasing copper mine resources. Our previous study investigated emission factors and total PCDD/F and polychlorinated biphenyl (PCB) emissions from secondary copper metallurgy in China (Ba et al., 2009). A large variation in PCDD/F and PCB concentrations (maximum concentration more than 1000-fold higher than the minimum) was observed over the range of 0.043–15.8 ng I-TEQ Nm^{-3} and 0.0003–0.126 ng WHO-TEQ Nm^{-3}, respectively. Similar results were also found for other countries and regions (UNEP, 2005; US-EPA, 2006; Yu et al., 2006; Wielgosinski et al., 2011). However, previous studies focused mainly on the estimation of emission factors and total amount of PCDD/F and PCB emitted from secondary copper smelters, and the reasons for the large variation in PCDD/F and PCB emission concentrations were not analyzed and discussed further.

In the secondary copper smelting process, there are distinctly different smelting stages. Some secondary smelters perform all purification stages using reverberatory furnaces or converters, while some plants purify the scrap in the reductive atmosphere of a blast furnace and then purify the charge in the oxidizing atmosphere of a converter (US-EPA, 2006). Although various different furnaces may be used in different secondary copper smelters, there

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* Corresponding author. Tel.: +86 10 62849172; fax: +86 10 62923563.
E-mail address: zhengmh@rcees.ac.cn (M. Zheng).

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Table 1
Basic information on the plants investigated.

Plant denotation	Production per furnace (ton)	Raw materials	APCS
TD	110	Copper scrap (100%)	BFs[a]
HP	120	Copper scrap (10%), blister copper (80%) and ACRE[b] (10%)	–
YF	180	Copper scrap (30%), blister copper (50%) and ACRE (20%)	BFs
WF	65	Blister copper (100%)	BFs

[a] Bag filters.
[b] Anode copper remains after electrolysis.

are usually three main smelting stages: feeding-fusion (FF), oxidation (OX) and deoxidization (DO). The raw materials are added firstly into the furnace heated by the combustion of fuel. When the raw materials have almost melted, air is blown through the copper liquid layer to purify the copper scrap. Finally, the reductant is injected into the copper liquid layer to deoxidize the copper. At each smelting stage, the formation and emissions of PCDD/F and PCB may occur as a result of the incomplete combustion of organic impurities in the raw material, fuel or reductant (such as coal). Furthermore, the formation of PCDD/Fs and PCBs can be catalyzed by copper. PCDD/F and PCB emissions and characteristics at different smelting stages may differ based on the operating conditions and feed materials used during the secondary copper smelting process. Therefore, it is essential that intensive studies be performed to investigate PCDD/F and PCB emissions and characteristics from different smelting stages in the secondary copper smelter.

In this study, stack gas samples were collected at different smelting stages from four plants to investigate the variation in PCDD/F and PCB emissions and characteristics during the secondary copper smelting process. The results should improve the understanding of dioxin emissions in secondary copper metallurgy.

2. Materials and methods

2.1. Sample collection

The reverberatory furnace is accepted as the traditional technology for secondary copper production in China as a result of its simple structure, ease of operation and suitability for large scale production. In the plants investigated in this study, copper smelting was performed in the reverberatory furnace and consisted of the three main stages mentioned in the introduction section. Heavy oil was used as fuel to melt the raw materials and the reductant was fine coal. Four typical plants in China (denoted TD, HP, YF and WF, see additional information in Table 1) were selected based on their differing raw material compositions. The raw materials from the TD and WF plants were pure copper scrap and blister copper, respectively. The copper scrap content in the raw materials at the YF and HP plants was 30% and 10%, respectively. In addition, a proportion of blister copper and anode copper remains after electrolysis existed in the raw materials at the HP and YF plants. Bag filters were used as the air pollution control system (APCS) in the sampled plants except for the HP plant, which was not equipped with an APCS.

Stack gas samples at different smelting stages were collected by an automatic isokinetic sampling system, Isostack Basic (TCR TECORA, Italy), according to EN 1948 from the four plants. The sampling system consisted of a filter (silica glass microfiber thimble, Whatman), followed by a condensing system and adsorbing trap containing resin (Amberlite XAD-2, Supleco). The resin was spiked with $^{13}C_{12}$-labelled surrogate standards (Wellington Laboratories, Canada) before sampling. Fly ash samples were collected simultaneously from the bag filters at the TD, YF and WF plants.

2.2. Sample preparation and analysis

Analysis of PCDD/Fs and PCBs was carried out according to EN 1948 and US-EPA method 1668A. Briefly, stack gas samples were spiked with known amounts of the $^{13}C_{12}$-labelled PCDD/F and PCB internal standards mixture (Wellington Laboratories, Canada) and then Soxhlet extracted with 250 mL of toluene for approximately 24 h. The ash samples were pre-treated with 1 M L^{-1} HCl after being spiked with $^{13}C_{12}$-labelled internal standards. The acid was rinsed off using pure water, and the solid phase ash and liquid phase were obtained. The solid phase ash was Soxhlet extracted after being dried, the liquid phase was liquid–liquid extracted with dichloromethane, and finally, the two extracts were combined. The extracts were concentrated to approximately 1–2 mL using the rotary evaporator. The concentrated extracts were cleaned by acid silica gel, multi-layer silica gel and alumina columns. The samples were spiked with a mixture of $^{13}C_{12}$-labelled PCDD/F and PCB recovery standards before high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis. HRGC/HRMS measurements were carried out with an Agilent 6890 gas chromatograph coupled to a Waters Autospec Ultima mass spectrometer (Waters, USA), and a DB-5 capillary column (60 m × 0.25 mm × 0.25 μm, Agilent) was used. The HRMS was equipped with a positive electron impact (EI+) source. The selected ion monitoring analyzer mode was used with a resolving power of 10000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively.

2.3. Quality assurance and quality control

The recoveries of surrogate standard in the stack gas samples were 82–108% and met the analytical method requirement. The $^{13}C_{12}$-labelled PCDD/F and PCB internal standards were 61–111% and 68–122%, respectively, proving the validity of the sample treatment. In identifying the target compounds, three quality control criteria were used: (a) the matching of GC retention times to the corresponding $^{13}C_{12}$-labelled standard compounds; (b) the signal-to-noise ratio being greater than 3:1; and (c) the isotopic ratios between the quantitative and confirmation ions being within ±15% of the theoretical values. One blank sample was included in each batch of samples, which had been spiked with the same amount of internal standard as the samples. No target compounds were detected in the blank samples.

3. Results and discussion

3.1. Emissions of PCDD/F and PCB from different smelting stages

The concentrations of PCDD/F and dioxin-like PCB (dl-PCB) in the stack gas of the different smelting stages from the four plants were in the range of 0.009–1.29 ng I-TEQ Nm^{-3} and 0.003–0.13 ng WHO-TEQ Nm^{-3}, respectively (see Table 2). There was a large variation in PCDD/F and dl-PCB concentrations at different smelting stages from each plant investigated. To compare PCDD/F

Table 2
PCDD/F and dl-PCB concentrations in the stack gas of different smelting stages from four plants (ng Nm^{-3}).

Plant denotation	Smelting stages	PCDD/Fs			PCBs	
		∑2378-PCDD/F	∑I-TEQ	Ratio[a]	∑dl-PCB	∑WHO-TEQ
TD	FF	71.6	1.29	4.1	11.6	0.13
	OX	44.7	1.12	3.8	6.42	0.09
	DO	58.7	0.39	0.22	2.55	0.02
HP	FF	2.87	0.17	3.9	3.49	0.04
	OX	4.23	0.24	4.0	3.64	0.04
	DO	0.91	0.07	6.8	4.33	0.04
YF	FF	0.16	0.01	6.0	0.31	0.003
	OX	0.16	0.02	4.1	2.29	0.02
	DO	0.12	0.009	7.0	0.39	0.003
WF	FF	2.19	0.23	3.2	4.91	0.02
	OX	0.47	0.04	3.7	9.72	0.006
	DO	0.34	0.04	4.6	8.31	0.007

[a] Ratio calculated as ∑PCDF/∑PCDD.

and dl-PCB emissions from different smelting stages, the emission factor from each smelting stage was estimated by the corresponding PCDD/F or dl-PCB concentration, stack gas flow rates and copper capacity as follows:

$$\text{Emission factor (ng TEQ t}^{-1}) = [\text{TEQ in stack gas (ng TEQ Nm}^{-3}) \times \text{stack gas flow rate (Nm}^3\text{h}^{-1})]/\text{capacity of copper (t h}^{-1}) \quad (1)$$

Fig. 1 shows the PCDD/F and dl-PCB emission factors at the different smelting stages during the secondary copper smelting process from the four plants. The PCDD/F emissions were mainly from the FF stage, with the percentage contribution to total emissions (sum of emission factors of the three smelting stages) being 54–88%. At the FF stage, the raw materials would be melted by heat from the combustion of heavy oil via the spray gun at the top of the furnace. The raw materials would be added into the furnace in several batches, so incomplete combustion of the fuel or organic impurities in the raw materials may occur when the operating conditions are unsteady at the feeding stage. Studies have indicated that PCDD/Fs could be formed easily during the unsteady state in industrial thermal processes (Chyang et al., 2010; Wyrzykowska-Ceradini et al., 2011). Furthermore, the FF stage would take approximately 8 h with several rounds of feeding-fusion. Thus, it was observed that the smelting stage from which most of the PCDD/F emissions occurred in the secondary copper smelter was the FF stage.

At the OX stage, PCDD/F contributions to total emissions were only 8.1–39% (Fig. 1), although the concentrations of PCDD/F appeared to correspond with that of the FF stage (Table 2). At the FF stage, the furnace door was kept closed to protect against heat loss after feeding. Besides feeding, there were no other operations before the OX stage. Some organic impurities in the raw materials would still exist in the furnace at the OX stage as a result of insufficient mixing. To further remove impurities, compressed air was blown through the copper liquid layer. Various metal oxides (especially copper oxide) were also produced at this stage. A previous study suggests that chlorinated benzenes could be a direct precursor of PCDFs by the catalysis of copper oxide under oxidizing atmosphere (Nganai et al., 2011). Thus, PCDD/Fs may be formed in the presence of organic impurity residues and metal oxides be generated at the OX stage. This may be why the PCDD/F concentrations from the OX stage correspond with that of the FF stage (Table 2). However, the OX stage emission factor was lower than that of the FF stage after consideration of the stack gas flow rate and copper capacity.

Almost all impurities in the raw materials had been removed during FF and OX, but a certain amount of PCDD/Fs was also detected at the DO stage with the contribution to total emissions being 3.9–6.7% (Fig. 1). At this stage, the fuel supply (heavy oil) was stopped and the fine coal reductant was injected continuously into the copper liquid layer by compressed air. The coal burned rapidly at this high temperature (more than 1000 °C). To fully deoxidize copper, excessive amounts of fine coal were used, and the incomplete combustion of fine coal could be observed clearly. Therefore, incomplete combustion of fine coal could supply carbon source and PCDD/Fs may form in the flue or in the APCS where dust adhered to the equipment could provide catalysts and chlorine atoms. Similar processes were also reported in previous studies (Xhrouet and De Pauw, 2004; Liu et al., 2009; Lenoir et al., 2011).

Based on the above discussion, the difference in feed materials and operating conditions at different smelting stages led to the variation in PCDD/F emissions during the secondary copper smelting process. The PCDD/F emissions occurred mainly at the FF stage during the secondary copper smelting process.

For the dl-PCBs, the contributions to total emissions were 28–71%, 11–68% and 3.4–13% at the FF, OX and DO stages, respectively (Fig. 1). It can be seen that the dl-PCB emissions at the OX stage were higher than that of the FF stage at the HP plant and different from the distribution of PCDD/F emissions among the three smelting stages. This may be attributed to the different formation sites and synthesis pathways between the PCDD/Fs and dl-PCBs.

3.2. PCDD/F and PCB homologue profiles from different smelting stages at the four plants investigated

To obtain a better understanding of the emission characteristics of PCDD/F and PCB from different smelting stages in the secondary

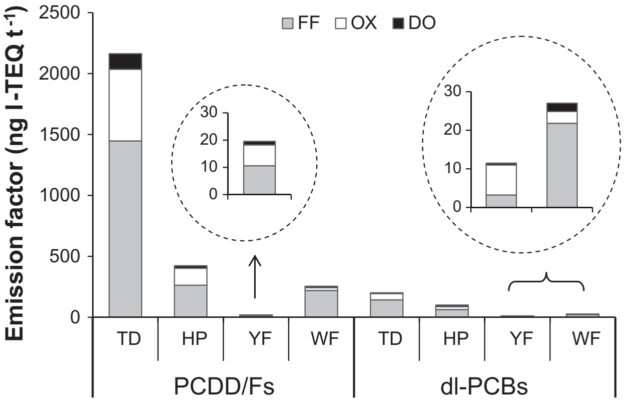

Fig. 1. PCDD/F and dl-PCB emission factors at different smelting stages during secondary copper smelting process from four plants.

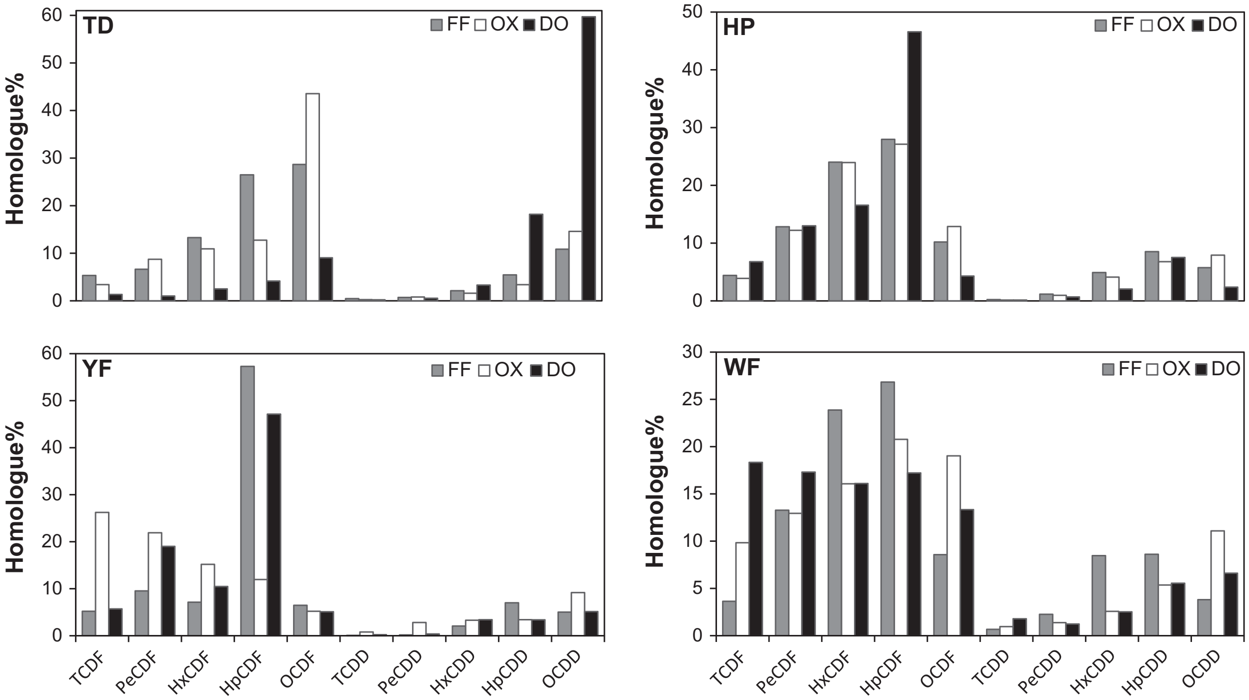

Fig. 2. Homologue distribution of PCDD/Fs (tetra- to octa-CDD/Fs) in the stack gas of different smelting stages from the four plants.

copper smelters investigated, the homologue profiles were analyzed for the tetra- to octa-CDD/Fs and tetra- to deca-CBs in the stack gas samples for the PCDD/Fs and PCBs, respectively. As shown in Fig. 2, the higher chlorinated PCDD/Fs were the main homologues for the TD, HP and YF plants. The weight distribution of PCDD and PCDF homologues increased with increasing degree of chlorination for the TD plant, and showed maxima at OCDF and OCDD, respectively. Similar homologue distribution trends as for the TD plant existed for the tetra- to hepta-CDD/F homologues at the HP and YF plants, but the relative proportions of OCDD and OCDF were lower than that of the TD plant. However, the trend was not observed for the distribution of PCDD/F homologues at the WF plant, because the proportions of PCDD/F homologues (tetra- to hexa-chlorinated) were relatively high. For the PCBs, the main homologues were observed as the lower chlorinated CBs and weight distribution decreased with increasing degree of chlorination (Fig. 3). However, the proportions of higher chlorinated PCB homologues were highest at the TD plant, followed by the YF and then the WF plants. It should be noted that raw stack gas was sampled in the HP plant because no APCS was present. As a result, the higher chlorinated homologues of PCDD/F and PCB, which are more likely to bind to particles, seemed to be more abundant in the stack gas of the HP plant. Besides the influence of the APCS, the difference in PCDD/F and PCB homologues distribution among different plants may be attributed to the variation in raw materials. The relative proportion of higher chlorinated homologues of PCDD/Fs (hepta- and octa-CDD/Fs) and PCBs (hepta- to deca-CBs) was consistent with the raw material copper scrap content for the TD (100%), YF (30%) and WF (0%) plants. A higher copper scrap content yielded a higher proportion of higher chlorinated homologues of PCDD/F and PCB in the stack gas.

The degree of chlorination is normally used to indicate the distribution of different chlorinated homologues (Everaert and Baeyens, 2002; Ba et al., 2009; Liu et al., 2009). To obtain a clearer indication of PCDD/F and PCB homologues distribution, the degree of chlorination of PCDD/Fs (tetra- to octa-CDD/Fs) and PCBs (tetra- to deca-CBs) in the stack gas from four plants is shown in Fig. 4. In general, the degree of chlorination of PCDD/Fs and PCBs at the TD, HP and YF plants, with copper scrap in the raw material, was higher than that of the WF plant, where the raw material consists entirely of blister copper. It is known that there are chlorinated organic compounds such as polyvinyl chloride (PVC) in the copper scrap (Sepulveda et al., 2010). In the thermal process, the higher chlorinated PCDD/Fs and PCBs would form preferentially in the presence of PVC (Gullett et al., 2007; Font et al., 2010). It is therefore clear that different raw material compositions can influence the emission characteristics of the PCDD/F and PCB in the secondary copper smelting process.

The ratio of furan/dioxin was calculated for every smelting stage from the four plants investigated. The furan/dioxin ratio was greater than 1 in all stack gas samples at the FF and OX stages (Table 2). In general, the ratio of furan/dioxin produced by de novo synthesis was greater than 1, but in the precursor formation, the furan/dioxin ratio was much smaller than 1 (Huang and Buekens, 1995; Tuppurainen et al., 1998; Everaert and Baeyens, 2002). Thus, it indicated that de novo synthesis was the main formation mechanism of PCDD/Fs at these two stages in the secondary copper smelters investigated. Interestingly, furan/dioxin ratio was 0.22 from DO stage at TD plant for its relative high proportions of hepta- and octa-CDDs (Fig. 2). A possible difference in reductant (fine coal) for DO stage at TD plant may be responsible for the different furan/dioxin ratio and it requires further research.

3.3. Influence of raw material composition on PCDD/F and PCB discharges

As concluded above, different raw material compositions can influence the PCDD/F and PCB homologue profiles in the stack gas from the secondary copper smelters investigated. We would like to determine whether the discharges of PCDD/F and PCB were affected by the raw material composition. Besides the stack gas, fly ash collected by the APCS was the main source of PCDD/F and PCB discharges from the secondary copper smelter and the discharges in the fly ash were usually higher than that in the stack gas (UNEP,

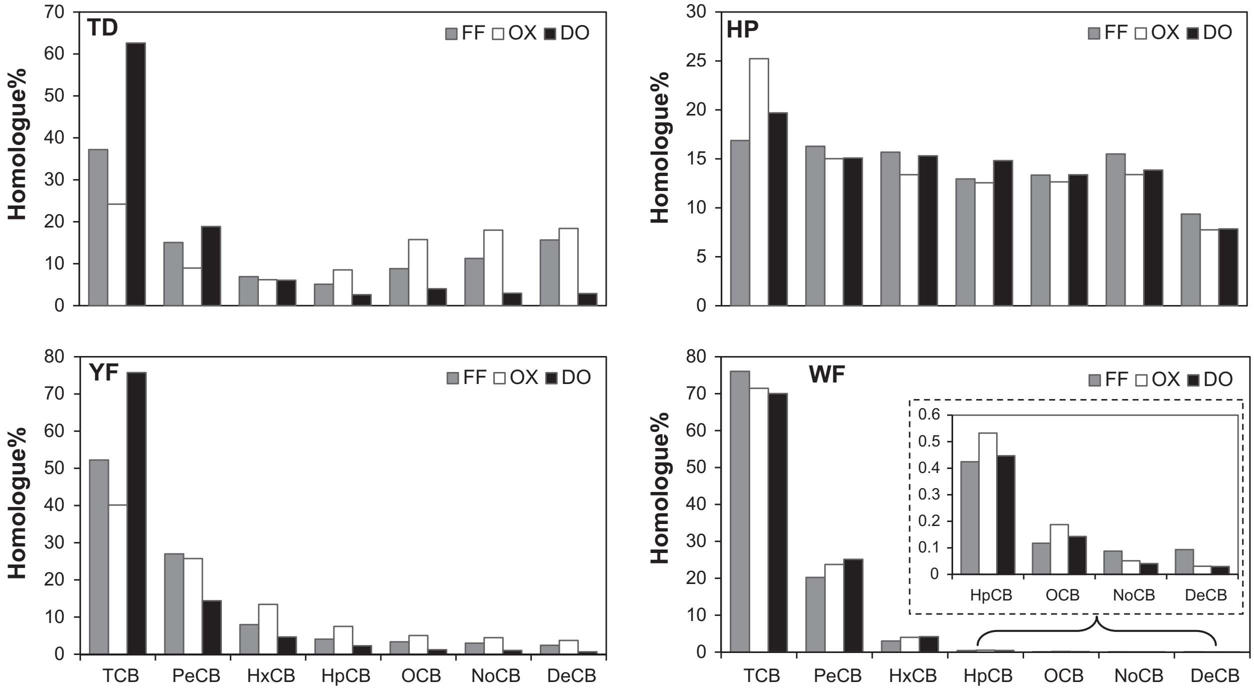

Fig. 3. Homologue distribution of PCBs (tetra- to deca-CBs) in the stack gas of different smelting stages from the four plants.

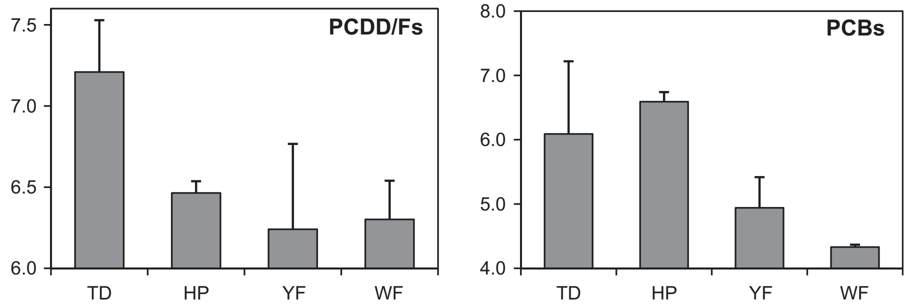

Fig. 4. Degree of PCDD/F and PCB chlorination in the stack gas from the four plants.

2005; Yu et al., 2006; Ba et al., 2009). Therefore, to evaluate the influence of raw material on discharges, the discharge factors of PCDD/F and dl-PCB in the fly ash were estimated for the TD, YF and WF plants as follows (the HP plant was not analyzed because no APCS existed at the plant and fly ash was not collected):

$$\text{Discharge factor in fly ash (ng TEQ t}^{-1}) = [\text{TEQs in fly ash (ng TEQ g}^{-1}) \times \text{product of fly ash (g h}^{-1})]/\text{capacity of copper (t h}^{-1}) \quad (2)$$

The PCDD/F and dl-PCB fly ash discharge factors were in the range of 5500–95 600 ng I-TEQ t^{-1} and 99.1–3860 ng WHO-TEQ t^{-1}, respectively, and were much higher than that of the stack gas emissions (Table A.3). Fortunately, the fly ash high in PCDD/F and dl-PCB concentrations was recycled as raw material to the primary copper smelter and not discharged into the environment. To obtain the total PCDD/F and dl-PCB discharge factors from the plants investigated, the sum of discharge factors in the fly ash and stack gas were calculated to be 102, 24.8 and 5.88 μg TEQ t^{-1} (Table A.3) for the 100%, 30% and 0% copper scrap contents from the plants investigated, respectively (Fig. 5). The total PCDD/F and dl-PCB discharge factors were consistent with the raw material copper scrap contents. The result implies that the raw material composition would significantly influence the total discharge. Therefore, the composition of raw material, especially the organic compound content (such as copper scrap) of the secondary materials should be

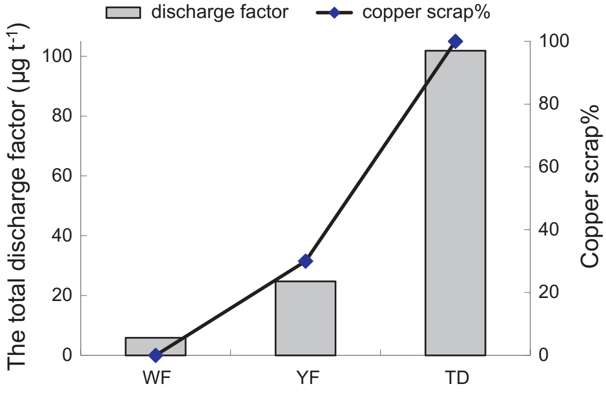

Fig. 5. Relation between PCDD/F and PCB total discharge factor (stack gas emission + fly ash discharge) and raw material copper scrap content from TD, YF and WF plants.

considered carefully when evaluating the PCDD/F and PCB emissions from secondary copper smelters.

4. Conclusion

The emissions and characteristics of PCDD/F and PCB from different smelting stages were investigated in four typical secondary copper smelters in China. FF stage was identified as main PCDD/F emission source from investigated secondary copper smelters. The PCDD/F and PCB homologue profiles showed different characteristics among the secondary copper smelters investigated for their different raw material compositions. In addition, it was found that the raw material composition can influence the total PCDD/F and PCB discharge significantly. These results could provide guidance to secondary copper smelter for implementing the best available technology and the best environmental practices to reduce dioxin emissions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.08.003.

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