Estimation and characterization of PCDD/Fs and dioxin-like PCB emission from secondary zinc and lead metallurgies in China

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Secondary zinc and lead production is addressed as one of the potential sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dioxin-like PCBs) due to the impurity of the raw material. However, the release inventory of PCDD/Fs and dioxin-like PCBs is very scarce for these secondary nonferrous metallurgies. This study selected typical secondary zinc and lead plants to investigate the emissions of PCDD/Fs and dioxin-like PCBs released from such plants in China. The toxic equivalent quantity (TEQ) emission factor of PCDD/Fs and dioxin-like PCBs released into the environment is higher for secondary zinc production, at 52 298.02 ng TEQ ton⁻¹ than for secondary lead production, at 646.05 ng TEQ ton⁻¹. The most abundant congeners of PCDD/Fs are 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF for the secondary zinc and lead metallurgies, respectively. The most abundant congener of dioxin-like PCBs in the samples collected from both metallurgies is CB-126. According to the distribution of PCDD/Fs (PCDF/PCDD >> 1) and the dominant contribution of higher chlorinated congeners, the *de novo synthesis* is assumed to be the main formation pathway of PCDD/Fs in the secondary zinc metallurgies. For the secondary lead metallurgies, the role of *precursor formation* is also very important. Based on the emission factor and production level, the total estimated emission amounts of PCDD/Fs and dioxin-like PCBs in both stack gas and fly ash released into the environment from secondary zinc and lead production is estimated to be at least 2.76 and 0.42 g TEQ yr⁻¹, respectively. The dioxin-like PCBs contribute 2.8% and 0.6% of the total emission from secondary zinc and lead plants, respectively.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are known to be some of the most toxic pollutants which could be produced as unintentionally produced persistent organic pollutants (UP-POPs) in many industrial processes.¹ Measures have to be taken to reduce the total releases of UP-POPs derived from anthropogenic sources, with the final goal being ultimate elimination.²

In recent years, there has been growing concerns around the UP-POPs inventory of metallurgy industries, especially the iron and steel metallurgy industry.^{3–6} However, information on the emission of UP-POPs from secondary nonferrous metal metallurgies is not enough although some conditions in the smelting process are suitable for formation of UP-POPs. These suitable conditions could be generally considered to be: (i) the elemental chlorine residing in the raw materials such as PVC, (ii) some types of nonferrous metal which could catalyze formation of UP-POPs, (iii) the proper temperature and oxygen concentration for formation of UP-POPs in some steps of the smelting process of secondary nonferrous metallurgy.^{1,7}

Although the smelting process in the secondary nonferrous metal metallurgy is addressed as one pathway in the formation of some UP-POPs, very little data about UP-POP emissions exist for the secondary zinc and lead metallurgies, this is probably due to

their lower production level in comparison to some other metals such as copper and aluminium.¹ Moreover, the data about emissions of dioxin-like PCBs from these secondary nonferrous metallurgies is not as common as that of PCDD/Fs. As part of a national UP-POP emissions inventory, this study focused on secondary zinc and lead production in China. The production levels of the secondary zinc and lead production in 2007 are 53 000 and 682 000 tons, respectively. Among the secondary lead plants, there are about 3 medium scale plants which contribute 3.3% to the total secondary lead yield in China. For the secondary zinc plants, the proportion of medium-sized enterprises is about 25% of the total secondary zinc yield in China.⁸ Based on the primary survey, two typical medium scale plants, with the necessary pollution control equipment, were selected from the secondary zinc and lead metallurgies in this study. The source-oriented method was adopted in the investigation of the emission of PCDD/Fs and dioxin-like PCBs from the secondary zinc and lead production. The calculation of total emission amounts is based on the emission factor achieved from the selected two plants and the production level of the secondary zinc and lead industries in China in 2007.

2. Materials and method

The smelting process of the secondary zinc production consists of feeding, melting, refining and casting in a crucible. For the secondary lead production, the smelting process consists of feeding, fusion, deoxidation, content adjusting, treatment of lead liquid and casting. The sampling in two types of metallurgies covered every step of the smelting process. The feeding and

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melting steps of secondary zinc production, as well as feeding and fusion steps of secondary lead production, got more attention because there are more organic parts containing residual chlorine in these steps than the latter steps.

For each plant, three stack gas samples and two fly ash samples were collected. Every stack gas sample from secondary zinc production corresponds to an entire smelting process. For secondary lead production, the first to third stack gas samples deal with the different steps and correspond to the feeding and fusion, treatment of lead liquid and casting, deoxidation and content adjusting. The sampling of stack gas was based on European method EN 1948 using an automatic isokinetic sampling system Isostack Basic (TCR TECORA, Italy). All the samples were collected in an upstream bag filter. Prior to collection, O₂, CO₂, H₂O and CO levels in the stack gas were measured to calculate the composition of the stack gas using flue gas analyzer GA-12 plus (Madur, Austria). The particles in the stack gas were trapped by a filter (25 mm id, 90 mm length) when the stack gas passed through the filter. The filter is made from a silica glass microfiber thimble bought from Whatman International Ltd (Whatman, UK). After a condensing system, the gas was adsorbed by a trap with amberlite XAD-2 resin purchased from Supelco International Ltd (VARINA, USA). According to the method EN-1948, isotope dilution techniques were used in this study. Before sampling, the resin was spiked with ¹³C₁₂-labelled surrogate standards to ensure the accuracy of the sampling. The fly ash samples were collected from the bag filter and/or quenching tower outlet during the stack gas sampling.

Both the stack gas and fly ash samples were spiked with a mixture of ¹³C₁₂-labelled PCDD/Fs and dioxin-like PCBs internal standards. The glass fiber filter and XAD-2 resin underwent Soxhlet extraction with toluene for 24 h. The fly ash samples were pretreated selectively with 2 M HCl, dried by air and underwent Soxhlet extraction with toluene for 24 h. Then, the extract was cleaned up by a concentrated sulfuric acid gel column, a multi-layer silica gel column and an alumina column. Before HRGC/HRMS analysis, the samples were spiked separately with ¹³C₁₂-labelled PCDD/Fs and dioxin-like PCBs recovery standards. HRGC/HRMS measurements were carried out with a Hewlett-Packard Model 6890 gas chromatograph coupled with an AutoSpec Ultima mass spectrometer (Waters, USA). For analysis of PCDD/Fs and dioxin-like PCBs, a DB-5 capillary column (60 m, 0.25 mm, 0.20 μm, Agilent J&W) was used. All dioxin-analytical grade solvents were purchased from Fisher Company (Thermo Fisher, USA). PCDD/F and dioxin-like PCB standards, including ¹³C₁₂-labeled homologues, were purchased from Wellington Laboratories (Ontario, Canada). For all determinations in this study, recovery of the internal standard was over 60%, proving the validity of the sample treatment; recovery of the surrogate spike was in the range of 70–80%, proving the high efficiency of gas sampling in this study.

3. Results and discussion

3.1. Characterization of PCDD/Fs emission from the secondary zinc and lead metallurgies

3.1.1 Congener profiles of PCDD/Fs in stack gas and fly ash of secondary zinc and lead metallurgies. The concentration

homologue distributions of PCDD/Fs in stack gas of secondary zinc and lead metallurgies are shown in Fig. 1. The stack gases 1–3 represent the 3 samples in the smelting processes of secondary zinc and lead metallurgies. For samples from secondary zinc plants, the figure named by ‘gas average’ depicts the average value of the three parallel samples. The pictures named by ‘gas total’ depict the integrated results of the whole processes of secondary lead smelting because the three samples are collected in different steps of the smelting process. It could be observed that the difference between the homologue distributions in the secondary zinc and lead metallurgies is obvious. In the stack gas from secondary zinc production, tetra-CDD/Fs (TeCDD/Fs) and penta-CDD/Fs (PeCDD/Fs) make the most important contribution to the concentration. However, for secondary lead production, the higher chlorinated PCDD/Fs like octa-CDD/Fs (OCDD/Fs) are the dominant homologues. Furthermore, in the fly ash from the secondary zinc and lead production, TeCDD/Fs and OCDD/Fs make the most important contribution to the concentration, respectively.

Fig. 2 presents the ratios of PCDF/PCDD ($R_{DF/DD}$) in stack gas and fly ash from the secondary zinc and lead metallurgies. For the formation of PCDD/Fs in large scale thermal processes, two major mechanisms have been proposed, *i.e.* pyrosynthesis or precursor formation and *de novo synthesis*. If the PCDF/PCDD ratio exceeds 1, the *de novo synthesis* may be the main formation mechanism of PCDD/Fs.¹⁰ It could be seen that the $R_{DF/DD}$ from tetra to octa CDD/Fs in the stack gas from secondary zinc production decreases from 2.06 to 0.34. The $R_{DF/DD}$ from Pe- to OCDD/Fs are close to or lower than 1. In contrast, $R_{DF/DD}$ from Te- to OCDD/Fs in the stack gas from secondary lead production increases from 2.09 to 15.92, and all of the $R_{DF/DD}$ are higher than 1. Generally, the integrated $R_{DF/DD}$ of the secondary zinc and lead production are 1.23 and 8.76, respectively. The $R_{DF/DD}$ of secondary lead production is higher than those obtained from other large scale thermal processes, such as incineration of municipal solid waste with the $R_{DF/DD}$ of 1.7 and wood combustion with the $R_{DF/DD}$ of 1.3, but lower than average $R_{DF/DD}$ of 9.5 in secondary nonferrous metallurgies.^{3,9,10} Moreover, the different trends of $R_{DF/DD}$ in the fly ash from two types of metallurgies could be also observed from Fig. 2. $R_{DF/DD}$ in fly ash from the secondary zinc metallurgy decreases from Te- to O CDD/Fs, and the OCDF/OCDD ratio is lower than 1. However, for the fly ash from the secondary lead metallurgy, the $R_{DF/DD}$ firstly decreases from Te- to HxCDD/Fs and then rises from Hx- to ODD/Fs, and all the $R_{DF/DD}$ are higher than 3.

The degrees of chlorination have been used to analyze the fingerprints of samples.¹⁰ It equals the sum of the product of the concentration percentage of the homologue multiplying the numbers of the substituted chlorine of the homologue. Fig. 3 shows that the chlorination degrees of PCDD/Fs vary from 4.66 (Zn gas) to 7.34 (Pb gas) in stack gas and fly ash from the secondary zinc and lead metallurgies. Such a high value of 7.34 for the chlorination degree in the stack gas from the secondary lead production further indicates that the concentration distributions of PCDD/Fs in the secondary lead metallurgy are dominated by higher chlorinated homologues.

3.1.2 TEQ of PCDD/Fs in stack gas and fly ash from the secondary zinc and lead metallurgies. Fig. 4 shows the mean TEQ

Fig. 1 The percentage contributions of homologue to the total concentration from TeCDD/Fs to OCDD/Fs in stack gas and fly ash from secondary zinc and lead metallurgies.

of PCDD/Fs in stack gas and fly ash samples collected from the secondary zinc and lead plants. The average TEQs of stack gas released from the secondary zinc and lead metallurgy are 98.02

and 0.35 ng TEQ (N m³)⁻¹, respectively. The corresponding TEQ ranges vary respectively from 78.98 to 153.88 ng TEQ (N m³)⁻¹ and from 0.053 to 0.727 ng TEQ (N m³)⁻¹. The mean TEQ of fly

Fig. 2 Concentration ratios of PCDF to PCDD ($R_{DF/DD}$) in stack gas and fly ash from secondary zinc and lead metallurgies.

Fig. 3 Analysis of the homologue concentration chlorination degrees for Te- to OPCDD/Fs in stack gas and fly ash from the secondary zinc and lead metallurgies.

ash samples is $5.64 \text{ ng TEQ g}^{-1}$ with a range of $4.66\text{--}6.62 \text{ ng TEQ g}^{-1}$ for secondary zinc production, and is $0.05 \text{ ng TEQ g}^{-1}$ with a range of $0.04\text{--}0.06 \text{ ng TEQ g}^{-1}$ for secondary lead production.

The TEQ congener patterns of PCDD/Fs in stack gas and fly ash are shown in Fig. 5. The abundance sequences are quite different for the samples from these two secondary metallurgies. The most abundant congener in stack gas from secondary zinc metallurgies is 2,3,4,7,8-PeCDF (36.1%), followed by 1,2,3,7,8-PeCDD (26.8%) and 2,3,7,8-TCDD (6.1%). For secondary lead metallurgies the sequence is 1,2,3,4,6,7,8-HpCDF (20.2%), followed by 2,3,4,6,7,8-HxCDF (17.2%) and 2,3,4,7,8-PeCDF (16.3%). The patterns are different from those reported for secondary zinc and lead metallurgies in Korea, which may be caused by differences in raw material.⁹

Fig. 4 The average level of PCDD/Fs and dioxin-like PCBs in TEQ format in stack gas and fly ash from the secondary zinc and lead metallurgies.

Fig. 5 The TEQ percentage contribution of the congeners of PCDD/Fs and dioxin-like PCBs in stack gas and fly ash from the secondary zinc and lead metallurgies.

3.2. Characterization of dioxin-like PCBs emission from secondary zinc and lead metallurgies

3.2.1 TEQ of dioxin-like PCBs in stack gas and fly ash of the secondary zinc and lead metallurgies. The mean TEQ of dioxin-like PCBs in stack gas and fly ash of secondary zinc and lead metallurgies are also shown in Fig. 4. The average TEQs of dioxin-like PCBs in stack gas released from secondary zinc and lead metallurgy are 2.786 and 0.002 ng TEQ (N m³)⁻¹ respectively. The TEQ ranges of dioxin-like PCBs of samples from secondary zinc and lead production are from 1.9 to 5.28 ng TEQ (N m³)⁻¹ and from 0.0009 to 0.005 ng TEQ (N m³)⁻¹ respectively. The mean TEQ of dioxin-like PCBs of fly ash released from secondary zinc and lead production are 0.0725 and 0.0002 ng TEQ g⁻¹, respectively. The TEQ ranges of dioxin-like PCBs of fly ash samples from secondary zinc and lead production are from 0.0329 to 0.1121 ng TEQ g⁻¹ and from 0.00007 to 0.0003 ng TEQ g⁻¹, respectively.

3.2.2 Congener profiles of dioxin-like PCBs in stack gas and fly ash of secondary zinc and lead metallurgies. The TEQ congener patterns of dioxin-like PCBs in stack gas and fly ash of secondary zinc and lead production are shown in Fig. 5. The most abundant congener is 2,2',3,3',4-PeCB (CB-126) in both metallurgies, followed by 2,2',3,3',4',4-HxCB (CB-169). The TEQ abundance ratios in the stack gas sample are 96.2% (zinc) and 96.3% (lead) for CB-126, and 3.1% (zinc) and 2.4% (lead) for CB-169. These two congeners together constitute more than 98% of total TEQ concentration of dioxin-like PCBs in stack gas samples. For fly ash, the most abundant congener is also CB-126 in both metallurgies, followed by CB-169. Their TEQ abundance ratios in fly ash are 96.1% (zinc) and 96.7% (lead) for CB-126, and 3.5% (zinc) and 2.5% (lead) for CB-169. These two congeners together constitute more than 99% of total TEQ concentration of dioxin-like PCBs in fly ash samples.

In contrast to PCDD/Fs congener patterns also shown in Fig. 5, the patterns of dioxin-like PCBs are very similar among four types of samples of stack gas and fly ash from secondary zinc and lead metallurgies. And the contribution of TEQ is attributed to almost one congener in all the samples collected. It resembles the result from Korea on dioxin-like PCBs emission from secondary zinc and lead metallurgies except that the contribution of CB-169 is higher.⁹ Additionally, this is also consistent with the studies on other thermal sources, such as municipal waste incineration, sintering and crematoriums.¹¹

3.3. TEQ emission amount (ng) of PCDD/Fs and dioxin-like PCBs from the selected secondary lead and zinc plants

The emission amount of PCDD/Fs and dioxin-like PCBs in stack gas from secondary lead and zinc production is shown in Table 1. The emission amount of 3 samples from secondary zinc production is very similar due to the collection from three same smelting processes. By contrast, the data of 3 samples from secondary lead production are quite different amongst each other. The emission amount of the first sample collected from the feeding and fusion step is much higher than the other two, accounting for 79.1% of the total emission of PCDD/Fs and dioxin-like PCBs in the smelting process of secondary lead. The rather high value suggests that the feeding and fusion step should get much more attention for pollution control.

3.4. The formation mechanism of PCDD/Fs and dioxin-like PCBs released from secondary zinc and lead metallurgies

For the formation of PCDD/Fs in large scale thermal processes, two major mechanisms have been proposed, *i.e.* pyrosynthesis or precursor formation and *de novo synthesis*. In the secondary lead metallurgy, the PCDF/PCDD ratio exceeds 1 and the homologue

Table 1 Total TEQ emission amount (ng) of PCDD/Fs and dioxin-like PCBs from the selected secondary lead and zinc plants

	Zn gas 1	Zn gas 2	Zn gas 3	Zn gas average	Pb gas 1	Pb gas 2	Pb gas 3	Pb gas total
PCDF	444 836	591 622	582 480	539 646	15 068	2193	1254	18 516
PCDD	319 818	404 064	387 033	370 305	1612	508	339	2460
Dioxin-like PCB	20 569	35 377	23 924	26 624	29.8	74.5	27.1	131
Total	764 655	995 687	969 513	909 952	16 680	2702	1594	20 977

and degree of chlorination in Fig. 1 and 3 point towards the dominant presence of higher chlorination homologues. These indicate that the *de novo synthesis* may be the main formation mechanism of PCDD/Fs. Moreover, the higher $R_{DF/DD}$ in this study, as compared to other studies,^{10,12} indicates that *de novo synthesis* is more likely to be the dominant formation mechanism of PCDD/Fs in the secondary lead metallurgy. In contrast, the importance of *precursor formation* and *de novo synthesis* in the formation of PCDD/Fs in the secondary zinc metallurgy is thought to be similar to each other because the ratio of PCDF/PCDD is close to 1 also with the dominant presence of the lower chlorinated homologue in the stack gas samples.^{10,12}

Based on the discussion in section 3.2.2, the congener patterns of dioxin-like PCBs from secondary lead and zinc metallurgies are similar to other thermal processes. It suggests that the formation mechanism of dioxin-like PCBs in the present two kinds of secondary metallurgies and from common thermal sources would be similar.¹³

3.5. Estimation of PCDD/Fs and dioxin-like PCBs emission factors and total release from secondary zinc and lead metallurgies in China

The following two equations were used to calculate the emission factors and total release for PCDD/Fs and dioxin-like PCBs:

$$\begin{aligned} \text{Emission factor of stack gas (ng TEQ ton}^{-1}\text{)} \\ = \frac{\text{TEQ of PCDD/Fs or dioxin-like PCBs (ng TEQ m}^{-3}\text{)} \times \text{dry stack gas flow rate (m}^3 \text{ step}^{-1}\text{)}}{\text{rate of metal production (ton step}^{-1}\text{)}} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Emission factor of fly ash (ng TEQ ton}^{-1}\text{)} \\ = \frac{\text{TEQ of PCDD/Fs or dioxin-like PCBs (ng TEQ g}^{-1}\text{)} \times \text{fly ash emission rate (g step}^{-1}\text{)}}{\text{rate of metal production (ton step}^{-1}\text{)}} \end{aligned} \quad (2)$$

$$\text{Total emission amount (g TEQ year}^{-1}\text{)} = \text{emission factor (ng TEQ ton}^{-1}\text{)} \times \text{activity level of reference year (ton year}^{-1}\text{)} \quad (3)$$

According to eqn (1) and (2), the TEQ emission factor of PCDD/Fs and dioxin-like PCBs released into the air is higher for secondary zinc production, at 52 298.02 ng TEQ ton⁻¹ than for secondary lead production, at 646.05 ng TEQ ton⁻¹. On the other hand, the PCDD/Fs and dioxin-like PCB emission factors released as fly ash from secondary zinc and lead production are calculated to be as low as 246.7 and 30.3 ng TEQ ton⁻¹, respectively. Such low emission factors could be attributed to the recycling of the fly ash in the plant for recovering the residual metal inside and the resultant small emission amount of the fly ash per ton of the product.

Subsequently, on the basis of eqn (3), the total emission amounts of PCDD/Fs and dioxin-like PCBs in the secondary zinc and lead metallurgies released to the environment are calculated to be 2.76 (zinc) and 0.42 g TEQ year⁻¹ (lead) where the dioxin-like PCBs take part of 2.8% (zinc) and 0.6% (lead) of the total TEQ. These values could be determined to be the minimum emission amount of PCDD/Fs and dioxin-like PCBs released from the secondary zinc and lead metallurgies in China

in 2007. The estimation of total emission amounts by emission factors developed in this study is based on the data of medium scale plants with the necessary pollution control equipment. The other smaller-sized plants in the secondary zinc and lead metallurgies in China were usually equipped with the simple and crude devices for the pollution control and could not even fulfill the requirements of isokinetic sampling. Therefore, the emission factors for smaller-scale plants are supposed to be higher than those summarized in this study and result in the higher emission amounts.

4. Conclusion

Emission of PCDD/Fs and dioxin-like PCBs from the secondary zinc and lead metallurgies in 2007 in China was evaluated in this study. The emission factor of the secondary zinc production is about 80 times higher than the secondary lead production. The congener patterns of PCDD/Fs from the secondary zinc and lead metallurgies are quite different from each other. Depending on these patterns, the formation mechanism of PCDD/Fs from secondary zinc and lead metallurgies may follow different pathways. For dioxin-like PCBs, the patterns are so similar that the formation mechanism may resemble each other. More investigations on the emission of PCDD/Fs and dioxin-like PCBs for the secondary zinc and lead industry in China need to be performed to obtain further information.

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