

COMPARING THE RELATIVE IMPORTANCE OF BROMINATED AND CHLORINATED DIOXINS IN EMISSION LEVELS FROM SECONDARY COPPER SMELTING PROCESSES

Liu GR^{1,2}, Li SM¹, Wang M¹, Jiang XX¹, Gao LR¹, Cai ZW², Zheng MH^{1,*}

¹ 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;

² Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China

* Corresponding author, E-mail: zhengmh@rcees.ac.cn

Introduction

Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) presents the similar properties and effects to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and have recently attracted increasing attentions. PBDD/Fs have been widely detected in various matrices such as air, sediments and human adipose samples¹⁻⁴. Study by Choi and coauthors⁴ indicated that the concentrations of PBDD/Fs in human adipose tissue samples collected in 1970 were significantly higher than that collected in 2000. The ratios of total tetra-brominated DD/DF to total tetra-chlorinated DD/DF in Japanese human adipose tissue have an obvious increase from 1970 to 2000. Jogsten et al.⁵ also analyzed the brominated and chlorinated dioxins in human adipose tissue and plasma samples, and reveal a contribution of brominated dioxins of up to 15% of the total dioxin TEQ. Thus, the relative importance of brominated dioxins compared to chlorinated dioxins have attracted increasing public concerns.

PBDD/Fs are unintentional byproducts formed during industrial thermal processes or impurities in brominated flame retardants (BFRs)⁶⁻⁹. Emission of PBDD/Fs from various industrial thermal processes consisted of waste incinerations and metallurgical processes have been reported^{2, 6, 10-12}. Study conducted by Du et al.⁶ implied that emissions of PBDD/Fs from metallurgical processes were much higher than that of waste incinerations. Secondary copper smelting has been identified to be an important industrial process of PBDD/F emissions in metallurgical sources in our previous study⁶. Thus, emissions of PBDD/Fs and PCDD/Fs from secondary copper smelting processes were investigated for the aim of evaluating the relative importance of PBDD/Fs compared to PCDD/Fs.

Materials and methods

In this study, a secondary copper smelting plant was investigated for the emissions of PBDD/Fs and PCDD/Fs. The main information and process techniques were briefly described below. The daily capacity was 110 ton per smelting furnace. The process of the investigated secondary copper smelting plant comprised feeding-fusion, oxidation, deoxidization and casting. Scrap coppers composed of recycled wires were the raw materials for secondary copper smelting. The air pollution control device (APCD) used in the investigated plant was bag filters.

Fly ash is an important matrix for catalyzing the formation of unintentional persistent organic pollutants (POPs) during industrial thermal processes^{13, 14}. Thus, fly ash was considered to be one of important release routes of unintentional POPs considering the high contamination levels of unintentional POPs were widely found in fly ash samples. In this study, fly ash sample was collected from the bag filters of secondary smelting process. The composition of fly ash is very important for understanding its catalytic effect¹⁵. In this study, the composition of fly ash was analyzed by X-ray fluorescence (XRF) for exploring the factors influencing the formation levels of PBDD/Fs and PCDD/Fs.

PBDD/F and PCDD/F congeners were qualified and quantified by isotopic dilution high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) method. The analysis of PCDD/Fs was performed according to the US EPA method 8290. The quantification and quantization of PBDD/Fs was carried

out according to our previous study with minor modifications⁶. Briefly, the fly ash samples were weighed and added ¹³C₁₂-labeled standards (EPA 1613 LCS and EDF 5382). Then, the samples were pretreated with 1 mol L⁻¹ HCl, and then were Soxhlet extracted with 250 mL of toluene for about 24 hours. The extractions were concentrated and were then subjected to a series of clean-up including multilayer silica gel column, basic aluminum column and carbon column. Finally, the extracts were reduced to about 20 μL by rotary evaporator and gentle nitrogen gas. ¹³C₁₂-labeled injection standards (EPA 1613 ISS and EDF 5383) were added into the corresponding fractions prior to instrumental analysis.

The identification and quantitation of PCDD/F and PBDD/F congeners were performed by an HRGC/HRMS by tracing the M⁺, (M+2)⁺, or the most intensive ions of the isotope cluster. A DB-5 column (15 m long, i.d. 0.25 mm, film thickness 0.10 μm) was employed to separate the 2,3,7,8-substituted PBDD/F congeners, and a DB5-ms column (60 m long, i.d. 0.25 mm, film thickness 0.25 μm) for the PCDD/F congeners. The injection volume was 1 μL. The mass range of MS was tuned and operated at around 10 000 resolution. Selected ion monitoring (SIM) mode was used for data acquiring.

Results and discussion

The composition of fly ash is very important for understanding its catalytic effect. The composition of fly ash was analyzed by XRF to explore the factors influencing the formation levels of PBDD/Fs and PCDD/Fs. The results of XRF analysis of the fly ash was shown in Figure 1. The copper and zinc have been widely recognized as the important element for catalyzing the formation of unintentionally produced POPs. It could be seen from Figure 1 that, CuO and ZnO were the major constituents of the fly ash with the fractions of higher than 20% (wt.%). The fraction of Cl with a value of 6.94% is about twice higher than that of Br (2.84%) in the fly ash.

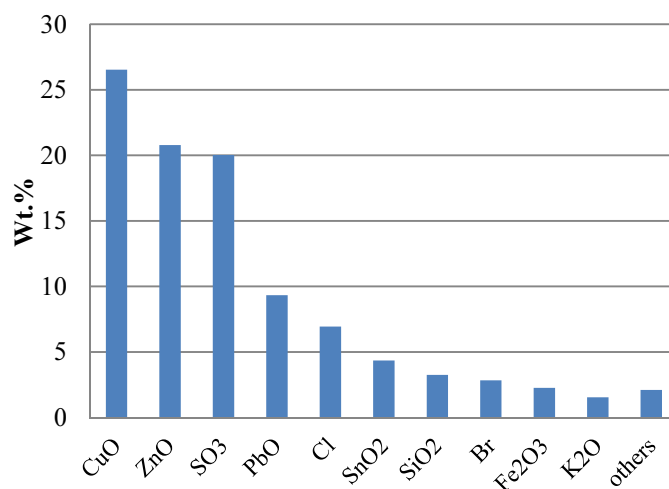


Figure 1. The XRF analysis of the fly ash from secondary copper smelting

Emissions of PCDD/Fs from secondary copper smelting have been intensively studied¹⁶⁻¹⁸. A large variation in PCDD/F concentrations (maximum concentration was about 1000-fold higher than the minimum) was observed¹⁶. The raw materials and APCD have been confirmed to be key factors influencing PCDD/F emission. The maximum emission of PCDD/Fs were observed for smelting plant with 100% of copper scrap as raw materials¹⁷. In this study, a plant with 100% of copper scrap as raw materials was selected as a extreme case for the purpose of evaluating the relative importance of PCDD/Fs and PBDD/Fs in their emission levels. The concentrations of seventeen PCDD/F congeners and eight PBDD/F congeners were listed in Table 1.

The accurate analysis of highly brominated dioxin congeners remains difficult. The hepta- and octa- brominated congeners were not determined in this study. From Table 1, the concentrations of PCDD/F congeners are extremely high with a range of 201-627 133 pg g⁻¹ for different congeners. While for PBDD/F congeners, the

concentrations ranged from 9.4 to 349 pg g^{-1} . The maximum concentration with a value of 349 pg g^{-1} was found for 2378-TBDF. For 2378-TCDF, the concentration was 4128 pg g^{-1} . The ratio of 2378-TBDF to 2378-TCDF was about 0.085. The ratios of brominated congeners to corresponding chlorinated congeners ranged from 0.0001 to 0.72, indicating a far lower concentrations for PBDD/F congeners than that of PCDD/F congeners. The contents of bromine or chlorine in the fly ash might correlate with the formation levels of PBDD/Fs and PCDD/Fs. However, the difference in PBDD/F and PCDD/F formation levels (up to four orders of magnitude) is not proportional to the ratio of Br to Cl in the fly ash. Thus, it is speculated that the extents of the influence of bromine and chlorine contents in the fly ash on the formation levels of PBDD/Fs and PCDD/Fs were significantly different.

Table 1. The congener concentrations of PCDD/Fs and PBDD/Fs in fly ash

PCDDs	Concentrations (pg g^{-1})	PBDD/Fs	Concentration (pg g^{-1})
2378-TCDD	201	2378-TBDD	145
12378-PeCDD	1410	12378-PeBDD	2.55
123478-HxCDD	2332	123478/123678-HxBDD	10.2
123678-HxCDD	4182		
123789-HxCDD	2972	123789-HxBDD	9.4
1234678-HpCDD	40462		
OCDD	236952		
2378-TCDF	4128	2378-TBDF	349
12378-PeCDF	8026	12378-PeBDF	179
23478-PeCDF	24603	23478-PeBDF	104
123478-HxCDF	26668	123478-HxBDF	3.67
123678-HxCDF	24565		
234678-HxCDF	44994		
123789-HxCDF	20336		
1234678-HpCDF	238138		
1234789-HpCDF	39767		
OCDF	627133		

There is currently no international consensus on the toxic equivalent factors of PBDD/F congeners compared to 2378-TCDD. The World Health Organization (WHO) ¹⁹ and other researchers ³ suggested an adoption of the I-TEF scheme of PCDD/Fs to enable the calculation of PBDD/F TEQ. Thus, the I-TEF scheme of PCDD/Fs is adopted for the corresponding PBDD/F congener to calculate the toxic equivalents (TEQ) of PBDD/F in this study. The TEQ of PBDD/Fs consisted of eight congeners was calculated to be 244 pg TEQ g^{-1} . While the TEQ of PCDD/Fs comprised of seventeen congeners was 30674 pg TEQ g^{-1} , the contribution of PBDD/Fs to the total TEQ of PBDD/Fs and PCDD/Fs is about 0.8%. Thus, the data obtained in this study suggested that the relative importance of PBDD/Fs is insignificant compared to PCDD/Fs in the emission levels from secondary copper smelting processes.

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References

1. Terauchi, H., Takahashi S., Lam P. K. S., Min B. Y., Tanabe S., (2009) *Environ. Pollut.*, 157: 724-730.

2. Gullett, B. K., Wyrzykowska B., Grandesso E., Touati A., Tabor D. G., Ochoa G. S., (2010) *Environ. Sci. Technol.*, 44: 394-399.
3. Li, H. R., Yu L. P., Sheng G. Y., Fu J. M., Peng P. A., (2007) *Environ. Sci. Technol.*, 41: 5641-5646.
4. Choi, J. W., Fujimaki S., Kitamura K., Hashimoto S., Ito H., Suzuki N., Sakai S., Morita M., (2003) *Environ. Sci. Technol.*, 37: 817-821.
5. Jogsten, I. E., Hagberg J., Lindstrom G., van Bavel B., (2010) *Chemosphere*, 78: 113-120.
6. Du, B., Zheng M. H., Tian H. H., Liu A. M., Huang Y. R., Li L. L., Ba T., Li N., Ren Y., Li Y. W., Dong S. P., Su G. J., (2010) *Chemosphere*, 80: 1227-1233.
7. Hanari, N., Kannan K., Miyake Y., Okazawa T., Kodavanti P. R. S., Aldous K. M., Yamashita N., (2006) *Environ. Sci. Technol.*, 40: 4400-4405.
8. Weber, R., Kuch B., (2003) *Environ. Int.*, 29: 699-710.
9. Hutson, N. D., Ryan S. P., Touati A., (2009) *Atmos. Environ.*, 43: 3973-3980.
10. Wang, L., Hsi H., Wang Y., Lin S., Chang-Chien G., (2010) *Environ. Pollut.*, 158: 1595-1602.
11. Wang, L. C., Chang-Chien G. P., (2007) *Environ. Sci. Technol.*, 41: 1159-1165.
12. Wyrzykowska, B., Tabor D., Gullett B. K., (2009) *Anal. Chem.*, 81: 4334-4342.
13. Addink, R., Espourteille F., Altwicker E. R., (1998) *Environ. Sci. Technol.*, 32: 3356-3359.
14. Cieplik, M. K., De Jong V., Bozovic J., Liljelind P., Marklund S., Louw R., (2006) *Environ. Sci. Technol.*, 40: 1263-1269.
15. Cobo, M., Galvez A., Conesa J. A., de Correa C. M., (2009) *J. Hazard. Mater.*, 168: 1223-1232.
16. Ba, T., Zheng M. H., Zhang B., Liu W. B., Xiao K., Zhang L. F., (2009) *Chemosphere*, 75: 1173-1178.
17. Hu, J., Zheng M., Nie Z., Liu W., Liu G., Zhang B., Xiao K., (2013) *Chemosphere*, 90: 89-94.
18. Yu, B. W., Jin G. Z., Moon Y. H., Kim M. K., Kyoung J. D., Chang Y. S., (2006) *Chemosphere*, 62: 494-501.
19. WHO, (1998) Environmental health criteria 205: Polybrominated dibenzo-p-dioxins and dibenzofurans. Geneva.