Estimation and congener specific characterization of PCNs emission from secondary nonferrous metallurgies in China

Bate, Minghui Zheng*, Bing Zhang, Wenbin Liu, Guijin Su, 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

Abstract
Secondary nonferrous production is addressed as one of the potential sources of unintentional produced persistent organic pollutants (UP-POPs) due to the impurity of raw material. However, the release inventory of polychlorinated naphthalenes (PCNs) is very scarce for these secondary nonferrous metallurgies. This study selected the typical secondary copper, aluminum, zinc and lead plants to investigate the emissions of PCNs released from secondary nonferrous production in China. In stack gas of secondary nonferrous production, the lower chlorination PCNs are the dominant homologues where Mono to Tri CNs make the most important contribution to the concentration. However, for fly ash, the higher chlorination PCNs like OCN is the dominant homologue.

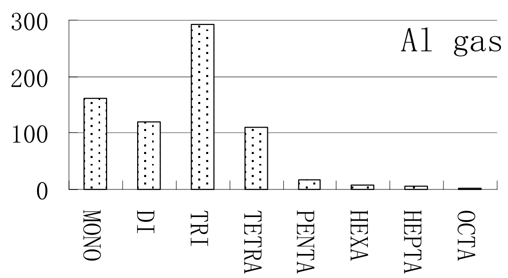
Introduction
PCNs are ubiquitous environmental pollutants that are structurally similar to polychlorinated dibenzo-pdioxins (PCDDs) and dibenzofurans (PCDFs). There are 75 possible congeners based on the naphthalene ring with one to eight chlorine atoms. It has been recognized that PCNs show dioxin-like toxicities because of their structural similarity to dioxins [1]. PCNs should be formed as a combustion by-product similar to PCDD/Fs, and dioxin-like polychlorinated biphenyls (dl-PCBs) [2]. PCNs have been detected in ashes and gases emitted from incinerators [3]. Measures have to be taken to reduce the total releases of PCNs derived from anthropogenic sources, and the final goal is ultimate elimination [4]**.** In recent years, there is a growing concern on UP-POPs released from metallurgy industries, especially iron and steel metallurgy industry [5]. However, information on the emission of PCNs 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 [6]. Although the smelting process in the secondary nonferrous metal metallurgy is addressed as one of the pathway of formation of some UP-POPs, very few data about the PCNs emission exist for the secondary nonferrous metallurgies. This study focused on the secondary copper, aluminum, zinc and lead production in China. The production level of these four kinds of secondary nonferrous production in 2007 is 5295000 tons. It takes parts of more than 99% of the total production level of secondary nonferrous metallurgy in China [7]. Based on the primary survey, eleven typical plants with the necessary pollution control equipments were selected from the secondary nonferrous metallurgies in this study.

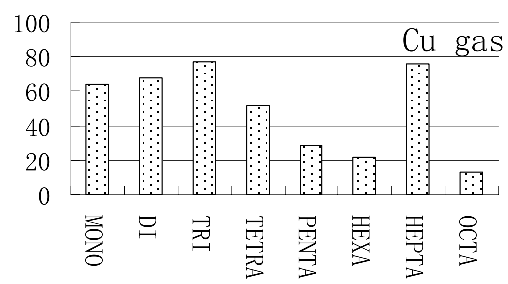
Materials and method

In this study, 11 plants were selected from secondary copper, aluminum, lead and zinc industries in China to investigate PCNs emission. The sampling in these metallurgies covered every step of the smelting process. The feeding and melting steps of secondary nonferrous production got more attention because there are more organic parts containing residual chlorine in these steps than the latter steps. The sampling of stack gas was based on Europen method EN 1948 using automatic isokinetic sampling system Isostack Basic (TCR TECORA, Italy). All the samples were collected at upstream of a bag filter. Prior to collection, O_2, CO_2, H_2O 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 particle in stack gas was trapped by a filter (25mm i.d., 90mm length) which is made by 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 Supleco International Ltd (VARINA, USA). The fly ash samples were collected from 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 $^{13}C_{12}$-labelled PCNs internal standards. The samples were pretreated selectively with 2 M-HCl, dried by air and carried out by Soxhlet extraction with toluene for 24 h. Then, the extract was cleaned up by concentrated sulfuric acid gel column, multi-layer silica gel column and alumina column. Before HRGC/HRMS analysis, the samples were spiked separately with $^{13}C_{12}$-labelled PCNs recovery standards. HRGC/HRMS measurements were carried out with a Hewlet Packed Model 6890 gas chromatograph coupled with an AutoSpec Ultima mass spectrometer (Waters, USA). For analysis of PCNs, 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). PCNs standards, including $^{13}C_{12}$-labeled congeners, were purchased from Cambridge Isotope Laboratories (Cambridge, USA). For all determinations in this study, recovery of the internal standard was over 60%, proving the validity of the sample treatment.

Results and Discussion

The homologue profiles of PCNs in stack gas and fly ash of secondary nonferrous metallurgies are shown in Fig 1. It could be observed that the difference between the homologue distributions in the secondary nonferrous metallurgies is obvious. In stack gas of secondary nonferrous production, the lower chlorination PCNs are the dominant homologues where Mono to Tri CNs make the most important contribution to the concentration. However, for fly ash, the higher chlorination PCNs like OCN is the dominant homologue.





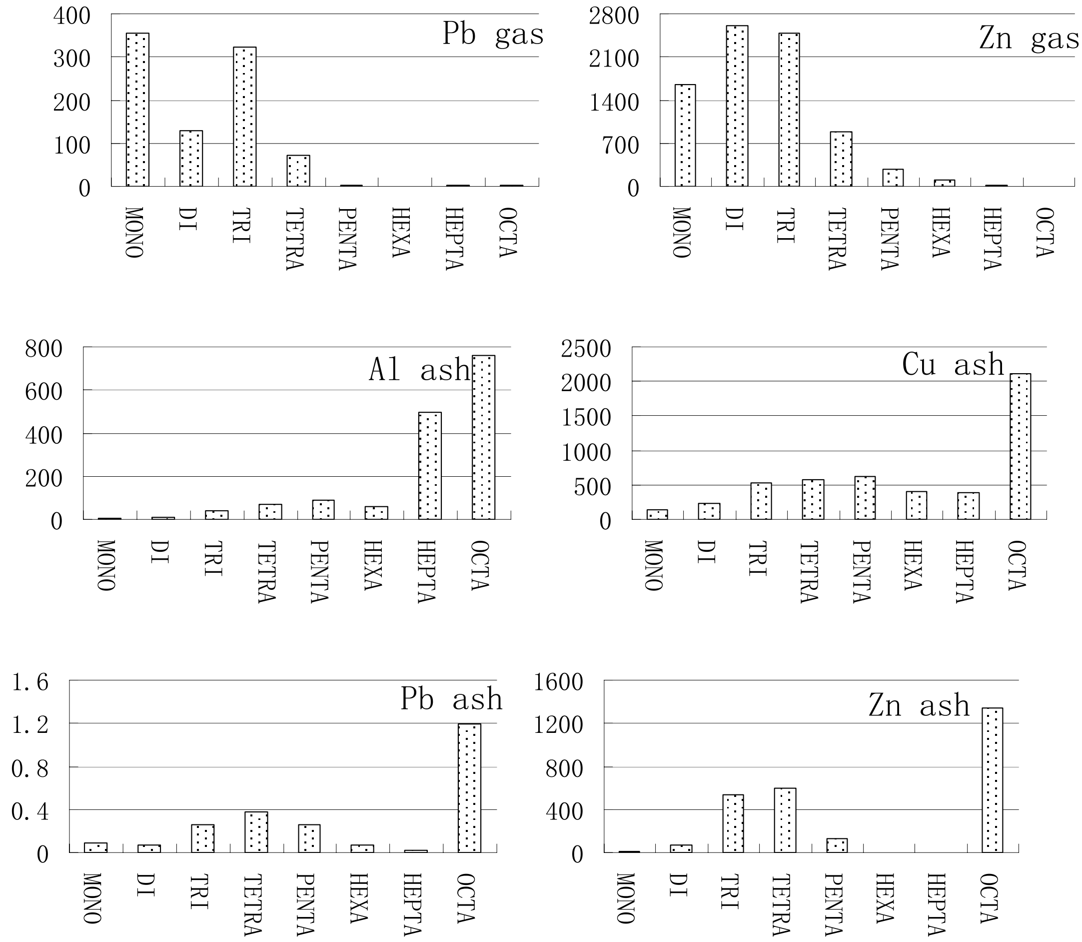


Fig 1 Homologue profiles of PCNs in stack gas and fly ash of secondary nonferrous metallurgies （*Unit: gas, ng $(Nm^3)^{-1}$; ash, ng g^{-1}）

The TEQ congener patterns of PCNs in stack gas and fly ash are shown in Fig 2. The abundance sequences are quite different for the stack gas samples from these secondary nonferrous metallurgies.

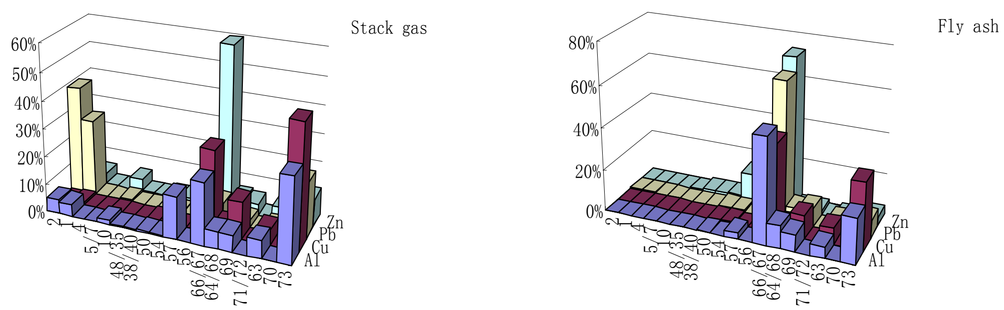


Fig 2 The TEQ congener patterns of PCNs and in stack gas and fly ash from the secondary nonferrous metallurgies

Acknowledgement

This study was supported by Chinese Academy of Sciences (Grant No. KZCX2-YW-420), National Natural Science Foundation of China (20677070, 20621703) and National 973 program (2009CB421606).

Reference

1.Falandysz, J., Environmental Pollution. 1998. 101(1): 77-90.
2. Imagawa, T., Lee, C.W. Chemosphere 2001. 44, 1511–1520.
3. Helm, P.A., Bidleman, T.F., Jantunen, L.M.M., Ridal, Organohalogen Compd, 2000. 47, 17–20.
4. Fiedler, H.Chemosphere, 2007. 67(9): S96-S108.
5. Anderson, D.R. and R. Fisher. Chemosphere, 2002. 46(3): 371-381.
6. UNEP, Standardized Toolkit for Identification and Quantification of Dioxin and Furan Release. 2005.
7.Association,C.N.-F.M.I..2008,Availablefrom:http://www.cnmn.com.cn/ShowNews.aspx?id=10144.