

# SPATIAL DISTRIBUTIONS OF ATMOSPHERIC EMISSIONS OF UNINTENTIONAL PERSISTENT ORGANIC POLLUTANTS FROM COKING INDUSTRIES IN CHINA

Liu GR, Zheng MH\*, Jiang XX, Wang M, Jin R, Zhao YY

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

\* Corresponding author. Tel.: +86 10 6284 9172

E-mail address: zhengmh@rcees.ac.cn (M. Zheng).

## Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HxCBz) and pentachlorobenzene (PeCBz) belong to the priority controlled persistent organic pollutants (POPs) covered under Stockholm Convention on POPs<sup>1,2</sup>. Polychlorinated naphthalenes (PCNs) have also been suggested to be included in the Annex C covered under Stockholm Convention<sup>3,4</sup>. Unintentional formation and release from industrial thermal sources are important sources of these several unintentional POPs. Polycyclic aromatic hydrocarbons (PAHs) have been considered as important precursors of unintentional POPs formation<sup>5,6</sup>. Since the occurrence of polycyclic aromatic hydrocarbons (PAHs) during coking processes, coke production have been speculated to be potential sources of unintentional POPs. Moreover, coke production have been confirmed to be one of important sources of unintentional POPs in China by field sampling and monitoring of stack gas and fly ash samples from coke plants in our previous studies<sup>1,7-9</sup>. It is significant to establish the atmospheric emission inventory of unintentional POPs with the aim of eliminating POP emissions<sup>10</sup>. In this study, the spatial distributions of atmospheric emissions of unintentional POPs from coking industries on province scale in China were presented and discussed. We hope this study could provide helpful information for understanding the regional emission contributions and developing control strategy for coking industries in China.

## Materials and methods

The field monitoring of PCDD/Fs, PCBs, PCNs, HxCBz and PeCBz in stack gas emissions from eleven coking plants in China have been carried out in our previous studies<sup>1,9</sup>. The emission factors of PCDD/Fs, PCBs, PCNs, HxCBz and PeCBz from the investigated coking plants have also been derived<sup>1,9</sup>. In this study, the average emission factors of several unintentional POPs were adopted for estimating the regional emission amounts from coking industries in China. The adopted average emission factors were 28.9 ng WHO-TEQ tonne<sup>-1</sup> for PCDD/Fs, 1.7 ng WHO-TEQ tonne<sup>-1</sup> for PCBs, 1.24 ng TEQ tonne<sup>-1</sup> for PCNs, 596 ng tonne<sup>-1</sup> for HxCBz, and 680 ng tonne<sup>-1</sup> for PeCBz, respectively<sup>1,9</sup>.

The data associated with the industrial activities of coke production in China in 2012 were obtained from the statistical data released by National Bureau of Statistics of China (NBSC)<sup>11</sup>. The emission amounts of unintentional POPs were estimated based on the emission factor and assuming a linear relation between the intensity of the activity levels and the emission amount. The emission amounts were calculated according to the

following equation:

$$\text{Emission amount} = \text{Activity level} \times \text{Emission factor}$$

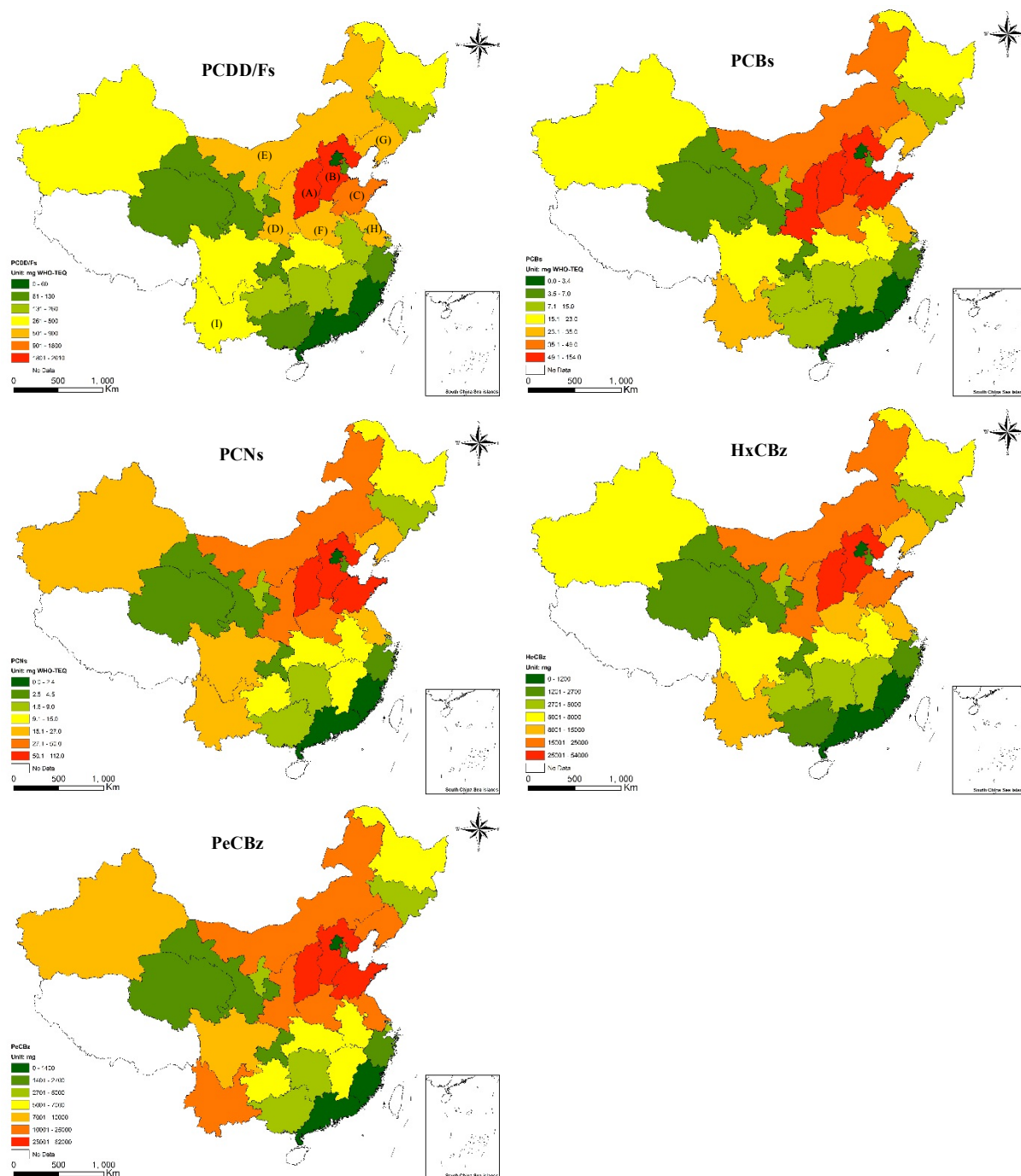


Figure 1. The spatial distributions of emissions of unintentional POPs to air from coking industries in different provinces of China in 2012

### Results and discussion:

Figure 1 demonstrated the spatial distributions of unintentional POPs in different provinces in China in 2012. It

could be seen from Figure 1 that several provinces around Shanxi and Hebei were the major emission sites of unintentional POPs from coking industries in China. Shanxi (A), Hebei (B) and Shandong provinces (C) were the main emission sites of PCDD/Fs from coking industries in China. The emission amount of PCDD/Fs from Shanxi provinces was higher than 1800 mg WHO-TEQ (World Health Organization-Toxic equivalents), followed by the Hebei and Shandong province with the emission amount in the range of 900-1800 mg WHO-TEQ. PCDD/F emissions from coking industries in Henan (F), Inner Mongolia (E) and Liaoning (G) ranged from 500 to 900 mg WHO-TEQ.

The TEQ of PCBs were calculated according to the toxic equivalent factors (TEF) recommended by WHO in this study<sup>12</sup>. The relative potency factors (REP) of PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) have been intensively studied<sup>13-15</sup>. Falandysz et al. recently summarized and updated the REP of PCN congeners relative to 2,3,7,8-TCDD<sup>16</sup>. In this study, the REPs of PCN congeners were used for the calculation of PCN TEQs. The unintentional PCB emissions from coking industries in four provinces including Shanxi, Hebei, Shandong, Shaanxi (D), were higher than 49 mg WHO-TEQ, followed by Inner Mongolia and Henan provinces with the emissions in the range of 35-49 mg TEQ. As regards PCNs, the emissions in Shanxi, Hebei and Shandong provinces were higher than 50 mg TEQ, followed by Shaanxi, Inner Mongolia and Henan provinces with the emissions in the range of 27-50 mg TEQ.

The emissions of HxCBz from coking industries in Shanxi and Hebei provinces were higher than 25 000 mg. The emissions in three provinces including Shandong, Shaanxi and Inner Mongolia were in the range of 15 000-25 000 mg. While for PeCBz, emissions from coking industries in Shanxi, Hebei and Shandong provinces were higher than 25 000 mg. The emissions of PeCBz from coking industries in Shaanxi, Henan, Inner Mongolia, Liaoning, Jiangsu (H) and Yunnan (I) provinces were in the range of 10 000-25 000 mg. Those results obtained this study could provide helpful information for understanding the regional emission contributions and developing control strategy for coking industries in China.

#### **Acknowledgements:**

We gratefully acknowledge support from the National 973 program (2015CB453100) and National Natural Science Foundation of China (21477147).

#### **References:**

1. Liu, G. R., Zheng, M. H., Liu, W. B., Wang, C. Z., Zhang, B., Gao, L. R., Su, G. J., Xiao, K., Lv, P. (2009) *Environ. Sci. Technol.*, *43*, 9196-9201.
2. Liu, G. R., Zheng, M. H., Cai, Z. W., Jiang, G.B., Wu, Y.N. (2013) *Trac-Trend Anal Chem*, *46*, 178-188.
3. Liu, G.R., Cai, Z.W., Zheng, M.H. (2014) *Chemosphere*, *94*, 1-12.
4. Liu, G. R., Zheng, M. H. (2013) *Environ. Sci. Technol.*, *47*, 8093-8094.
5. Weber, R., Iino, F., Imagawa, T., Takeuchi, M., Sakurai, T., Sadakata, M. (2001) *Chemosphere*, *44*, 1429-1438.
6. Iino, F., Imagawa, T., Takeuchi, M., Sadakata, M. (1999) *Environ. Sci. Technol.*, *33*, 1038-1043.
7. Liu, G. R., Liu, W. B., Cai, Z. W., Zheng, M.H. (2013) *J. Hazard. Mater.*, *261*, 421-426.
8. Liu, G. R., Zheng, M. H., Ba, T., Liu, W.B., Guo, L. (2009) *Chemosphere*, *75*, 692-695.
9. Liu, G. R.; Zheng, M. H.; Lv, P.; Liu, W. B., Wang, C. Z., Zhang, B., Xiao, K. (2010) *Environ. Sci. Technol.*, *44*, 8156-8161.

10. Fiedler, H. (2007) *Chemosphere*, 67, S96-S108.
11. NBSC (2015) National Bureau of Statistics of China, <http://www.stats.gov.cn/tjsj/>
12. Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. (1998) *Environ. Health Perspect.*, 106, 775-792.
13. Blankenship, A. L.; Kannan, K.; Villalobos, S. A.; Villeneuve, D. L.; Falandysz, J.; Imagawa, T.; Jakobsson, E.; Giesy, J. P. (2000) *Environ. Sci. Technol.*, 34, 3153-3158.
14. Villeneuve, D. L.; Kannan, K.; Khim, J. S.; Falandysz, J.; Nikiforov, V. A.; Blankenship, A. L.; Giesy, J. P. (2000) *Arch Environ Con Tox*, 39, 273-281.
15. Villeneuve, D. L.; Khim, J. S.; Kannan, K.; Giesy, J. P. (2002) *Environ Toxicol*, 17, 128-137.
16. Falandysz J; Fernandes A; Gregoraszcuk E; M, R. (2013) *Organohalogen Compd.*, 75, 336-338.