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Levels and Profiles of Unintentionally Produced Persistent Organic Pollutants in Surface Soils from Shanxi Province, China

G. R. Liu · M. W. Cai · M. H. Zheng · Z. Q. Nie · W. B. Liu · P. Lv · G. J. Su · L. R. Gao · K. Xiao

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Abstract Six species of unintentionally produced persistent organic pollutions comprised of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, polychlorinated biphenyls, polychlorinated naphthalenes, hexachlorobenzene and pentachlorobenzene in soils collected from Shanxi province, China were determined. The sum toxic equivalent ranged from 0.14 to 2.20 with an average of 0.94 pg TEQ/g. Polychlorinated dibenzo-p-dioxins/furans contributed the most toxic proportion to the total toxic equivalent. CB-126 was the most toxic contributor to polychlorinated biphenyls. CN66/67 and CN73 are the dominant toxic congeners to polychlorinated naphthalenes. From the patterns, it was speculated that thermal related industries were possible sources of unintentionally produced persistent organic pollutions.

Keywords POPs · Profile · Source · Surface soil

Polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz) belong to the typical persistent organic pollutions (POPs) covered under the Stockholm Convention. Polychlorinated naphthalenes (PCNs) were also selected as the candidate POP by UN-ECE POP protocol (Lerche et al. 2002). These POPs normally could be unintentionally produced during various anthropogenic activities and are often termed as unintentionally produced POPs (UP-POPs).

Many industries including coke plants, coal-fired power station, and steel-making plants are sources of UP-POPs (Bailey et al. 2009; Liu et al. 2009). There are many typical industries around central area of Shanxi province of China. However, few studies about the levels and profiles of UP-POPs in the environment media of Shanxi province were carried out. Surface soils are not only the sinks of UP-POPs, but also the sources of UP-POPs in the terrestrial environment (Ren et al. 2007). Investigation on the levels and profiles of UP-POPs in surface soil are very helpful for understanding their sources and risk exposure.

In this study, the surface soil samples from several central counties and cities of Shanxi province of China were collected, and the UP-POPs in samples were analyzed by isotopic dilution GC/MS technique. The primary aims of the present study were that: (1) determination of UP-POPs in the surface soils for understanding the contamination levels of UP-POPs in the central area of Shanxi province; (2) comparisons of toxic equivalents of the investigated POPs for learning about the toxic contribution of the investigated POPs; (3) presentation and discussion of profiles of these POPs, which might provide useful information for exploring the sources of UP-POPs in the investigated areas.

Materials and Methods

Fifteen surface soil samples from six counties and cities around central area of Shanxi province were collected. Each composite soil sample was around 8 sub-samples

G. R. Liu (✉) · M. W. Cai · M. H. Zheng · Z. Q. Nie · W. B. Liu · P. Lv · G. J. Su · L. R. Gao · K. Xiao
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 100085 Beijing, China
e-mail: grliu@rcees.ac.cn

M. W. Cai
College of Resources and Civil Engineering, Northeastern University, 110819 Shenyang, China

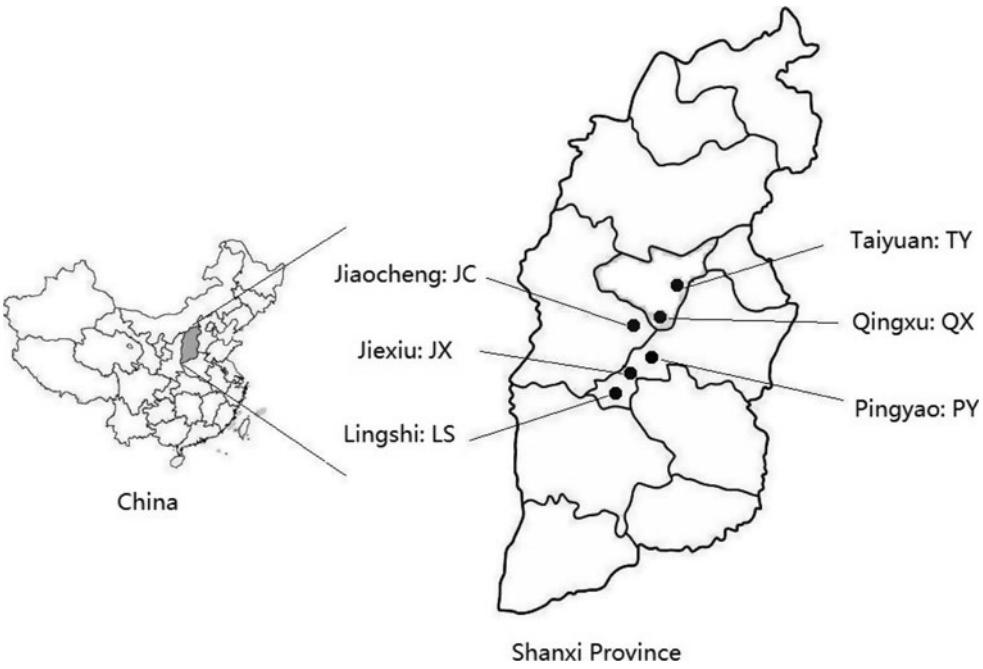

Fig. 1 Sampling locations for the investigated area

from sampling sites. The locations of six counties and cities for sampling soil were described in Fig. 1.

The analysis of PCDD/Fs and dl-PCBs was carried out based on US EPA method 1613B and 1668A modifications. Briefly, the samples were spiked with $^{13}C_{12}$-labeled internal standards, and then were extracted by accelerated solvent extraction (ASE) with mixture solution of n-hexane and dichloromethane. Then, the concentrated extract was purified by multilayer silica gel columns. PCDD/Fs and PCBs were fractionated by basic alumina columns. Prior to injection, $^{13}C_{12}$-labeled injection standards were added into corresponding fractions for calculation of recoveries. Analysis of dl-PCBs and PCDD/Fs were performed by HRGC/HRMS.

Analysis of PCNs in the soils samples were carried out by HRGC/HRMS method. The detail procedure of exaction, cleanup and instrumental analysis of PCNs has been presented in the reference (Guo et al. 2008). With regard to the analysis of HxCBz and PeCBz, the samples were spiked with known amount of $^{13}C_6$-PCBz (Cambridge isotope chlorobenzene cocktail Tetra/Pentra/Hexa isomers, EM-1725-A). The soil samples were extracted by ASE with mixture solution of n-hexane and dichloromethane, and then were purified with multilayer silica gel columns. Analysis of HxCBz and PeCBz was carried out by an Aglient 6890 GC interfaced to 5973 N MSD. $^{13}C_6$-HxCBz and $^{13}C_6$-PeCBz was used as isotope internal standard for quantitative determination of HxCBz and PeCBz.

For quality control, peaks were identified based on the retention time compared to available ^{13}C-labeled internal standards, and the isotope ratios of the two monitored ions for each compound had to be within 15% of the theoretical values. The limit of detection ranged from 0.1 to 8.9 pg/g. The recoveries of ^{13}C-labelled internal standards ranged from 36% to 132%.

Results and Discussion

The concentrations and TEQ of the selected UP-POPs in soil samples were described in Fig. 2. For congeners with concentrations below LOD, a value of LOD/2 was assigned for the calculation of total concentration and TEQ. The TEQs of PCNs and HxCBz were calculated according to the TEFs reported by Guo et al. (Guo et al. 2008) and van Birgelen et al. (van Birgelen 1998), respectively.

In this study, the total TEQs of PCDD/Fs, dl-PCBs, PCNs and HxCBz in the investigated soil samples ranged from 0.14 to 2.20 pg TEQ/g. The average concentration and TEQ of PCDD/Fs in surface soil samples were 8.44 pg/g and 0.56 pg WHO-TEQ/g, respectively. Zheng et al. (2008) summarized the environmental levels of PCDD/Fs pollution in China. From the results obtained in this study, the PCDD/Fs levels in surface soil were far lower than that of electronic waste recycling sites, vicinity of pentachlorophenol factory, and schistosomiasis disease area of China, and were comparable to those from mountain, farmland, and urban area (Zheng et al. 2008). As for PCBs, study on the dl-PCBs in surface soil was very lacking. The average concentration and TEQ of dl-PCBs in surface soil samples in this study were 186 and 0.07 pg

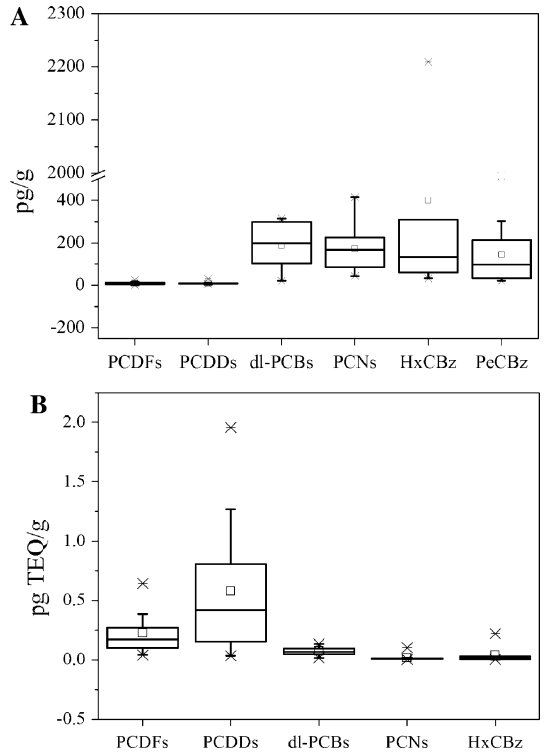

Fig. 2 Concentrations **a** and TEQ **b** of the UP-POPs in the soil samples

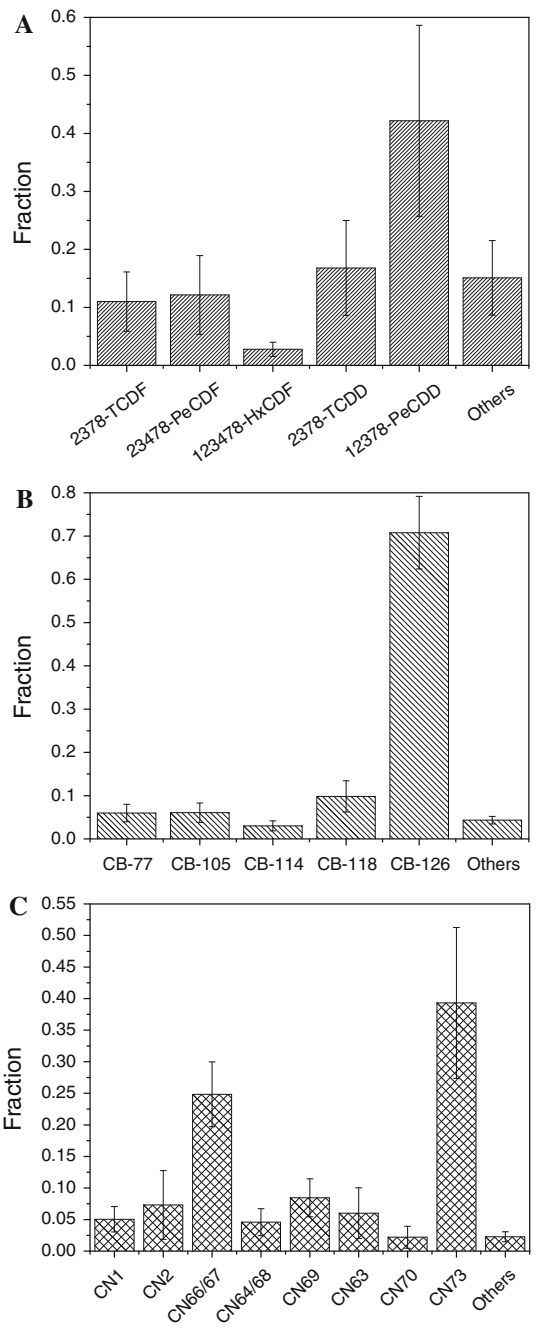

Fig. 3 TEQ pattern of PCDD/F **a**, dl-PCB **b** and PCN **c** congeners

WHO-TEQ/g, respectively, which were comparable to those of other urban cities (Wang et al. 2008).

PCNs as candidate POP has been proposed for inclusion in UN-ECE POP protocol (Lerche et al. 2002), and the environmental levels of PCNs have aroused public's attention. However, intensive investigation on PCN levels in soil samples in China have not been carried out. In this study, the average concentration and TEQ of PCNs in soil samples were 172 pg/g (range: 45–414 pg/g) and 0.02 pg TEQ/g (range: 0.01–0.1 pg TEQ/g), respectively. These levels were far lower than the concentrations of PCNs in soils collected from the site near to chlor-alkali plant (Kannan et al. 1998).

Meijer et al. (2003) studied HxCBz concentrations in background surface soils collected from 191 locations around the world, and the average concentration was 0.68 ng/g dw. Very high HxCBz concentrations were detected in surface soils from industrial area in vicinity of an organochlorine producing factory (Barber et al. 2005). The concentrations of HxCBz in the surface soils investigated in this study ranged from 33 to 2,209 pg/g with an average value of 400 pg/g, which were slightly lower than the global mean background concentration in 1998, and were far lower than that of vicinity of an organochlorine producing factory.

Sources and environmental levels of PeCBz have recently aroused public's attention due to its inclusion into the Stockholm Convention on POPs. However, investigation on PeCBz level in environmental media was rarely carried out. The concentrations of PeCBz in the soil samples investigated in this study ranged from 21 to 522 pg/g with an average of 144 pg/g, which were comparable with the reported level by Bailey et al. (2009).

The TEQ pattern of PCDD/F, dl-PCB, and PCN congeners were presented in Fig. 3. It could be seen that 12378-PeCDD, 23478-PeCDF, 2378-TCDD, and 2378-TCDF were the dominant contributors to the TEQ of

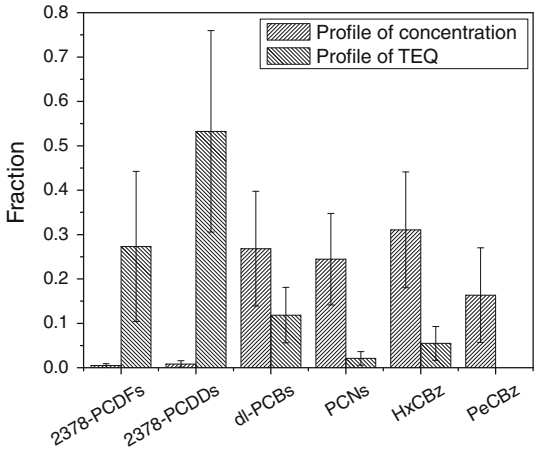

Fig. 4 Concentration and TEQ profiles of the UP-POPs

PCDD/Fs due to their relatively high TEFs compared with other PCDD/F congeners. For dl-PCBs, CB-126 was the most dominant contributor due to its high TEF compared with other dl-PCB congeners. With regard to PCNs, CN66/67 and CN73 are the dominant congeners to the TEQ of PCNs due to its high TEFs compared with other PCN congeners. The ratio of CN73 to CN74 ($R_{73/74}$) vary in different source samples, with values lower than 1 (range: 0.2–0.4) in Halowaxes mixtures, while higher than 1 in stack gas or fly ash samples from thermal related sources (Guo et al. 2008). Thus, the ratios of CN73 to CN74 have been used to indicate possible sources of PCNs (Guo et al. 2008). In this study, the ratios of CN73 to CN74 ranged from 2.7 to 11.6 with an average of 6.6 in surface soil samples, which indicate that thermal related processes might be the dominant sources of PCNs in the surface soils.

The concentration and TEQ profiles of the investigated POPs in the soils were presented in Fig. 4. Although the concentrations of PCDD/Fs were far lower than that of other investigated POPs, the TEQ contribution of PCDD/Fs to the total TEQ of the investigated POPs were higher than 50%, which caused by the relatively much higher TEFs of PCDD/Fs than that of other investigated POPs. The TEQ comparison of the investigated POPs showed that PCDD/Fs are still the dominant toxic contributor in surface soils from the investigated area, followed by dl-PCBs.

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