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Distribution and Characterization of Higher Chlorinated Benzenes in Outdoor Dust Collected from a Fast Developing City in North China

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Abstract Five higher Chlorinated Benzenes (CBs), include Hexachlorobenzene (HCB), pentachlorobenzene (PeCB) and three isomers of tetrachlorobenzens, were analyzed in 20 outdoor dust samples collected from a fast developing city, Xinxiang. Only HCB was detected in all outdoor dust samples. The dominate part of the CBs residue in most samples was HCB and the mean HCB concentration (4.13 ng/g dry weight) in this study was in the range of global background soil HCB levels (ranging from 0.010 to 5.20 ng/g dry weight). The higher ratios of HCB/PeCB in the outdoor dust samples in the present study indicate that pesticide application may be an important source of HCB in China.

Keywords Chlorinated benzenes · Outdoor dust samples

Chlorinated Benzenes (CBs) are isomeric chlorinated aromatic compounds having a benzene ring that is substituted with 1–6 chlorine atoms. Environmental contamination with CBs is widespread due to the importance of these chemicals as industrial intermediates, pesticides and solvents. Besides, CBs can be generated inadvertently as by-products during various incomplete combustion processes (Oh et al. 2007). Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) have been included as persistent organic pollutants (POPs) by the Stockholm Convention. By now, CBs have become ubiquitous pollutants in the environment (Fu et al. 2008). The best estimate of global HCB emissions from various sources are as follows: pesticide application, manufacturing and combustion including biomass burning (Bailey 2001). Global emissions of PeCB around the year 2000 are clearly dominated by combustion sources. Of all sources, combustion of biomass, combustion of solid waste and combustion of coal represent the three largest emissions. Industrial sources are relatively minor (Bailey 2007).

Xinxiang city is located in the north of Henan province, China. The continental climate of the North Temperate Zone here is characterized by four distinct seasons, with a cold winter and a hot summer besides a comparatively moderate spring and autumn. The annual average temperature here is 14.6°C. Similar with a lot of towns in China, in the past 30 years, Xinxiang city lived a fast developing phase with the city built-up area from 34.2 km^2 to about 100 km^2 and the population from about 350,000 to over 1,000,000. With the development of industry in recent years, Xinxiang has provided increasing amounts of chemical, electron and metal products. The rapid industrialization and urbanization have brought evident environmental pollution. For example, Beijing had resulted in 20 times of HCB increase from 1980s to 2005 (Dai et al. 2008). As facile "environmental media", dusts were used to investigate the distribution of POPs in living surroundings (GRL 2001). But there are few reports on the CBs distribution in deposition or dust. CBs are more hydrophobic with increasing number of chlorine substituents. Based on their properties, lower chlorinated benzenes have a tendency to become volatilized, whereas higher chlorinated benzenes have a tendency to become sorbed on soil and sediment particles.

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The purpose of this study was to investigate the distribution and characterization of higher chlorinated benzenes [include HCB, PeCB and tetrachlorobenzens (TeCBs)] in the outdoor dust of a fast developing city, Xinxiang, in order to evaluate the potential risk to human health and to identify the possible sources of CBs pollution.

Materials and Methods

HCB, PeCB and three isomers of TeCBs standards were purchased from Aladdin reagent Database Inc. (Shanghai China). 2,4,5,6-Tetrachloro-m-xylene (TCMX) was purchased from Supelco (Bellefonte, PA, USA) and was used as a surrogate standard. The standards were further diluted to the desired concentration with isooctane and used as working standards. Hexane, dichloromethane used for the extraction and cleanup procedures were pesticide grade (J. T. Baker, USA), and other solvents and reagents were of analytical grade. Silica gel (100–200 mesh, analytical grade) was activated in a drying oven at 130°C for 16 h and then cooled down to room temperature in a desiccator. Anhydrous sodium sulfate (analytical grade) was heated at 600°C for 12 h to destroy organic contaminants before use.

In the city built-up area, there are lots of outdoor hardened grounds, such as the commercial street, city square, porch of the house, concreted road and so on. In this study, we classified these hardened grounds into three styles: (1) park area, include school and park; (2) living area, include habitation block, commercial street and hospital; (3) industrial park. In May 2010, 20 outdoor dust samples were collected from various style hardened grounds of Xinxiang (Table 1). In each sample, about 4 square meters hardened ground was wiped by pre-cleaned cotton to collected outdoor dust. The dust samples were transferred directly into pre-cleaned aluminium foil envelopes. Then they were preserved frozen at −20°C until analysis.

In the laboratory, about 1 g of each dust sample was ground with 5 g anhydrous sodium sulfate into a free-flowing powder. The samples were extracted with 30 mL of hexane/dichloromethane (1:1, v/v) by ultrasound for 4 min, and the extracts were then separated by centrifugation. This process was repeated three times. Before extraction, 2,4,5,6-tetrachloro-m-xylene (TCMX) was added as a surrogate standard.

Table 1 Classification of the outdoor dust samples

Style	Sample number
Park area	CB-9, CB-10, CB-14, CB-20
Living area	CB-1, CB-4, CB-6, CB-7, CB-8, CB-12, CB-13, CB-19
Industrial park	CB-2, CB-3, CB-5, CB-11, CB-15, CB-16, CB-17, CB-18

The extracts were concentrated, and solvent-exchanged to hexane and purified on an 20 mm i.d. silica column packed, from the bottom to top, with neutral silica (4 g, 3% deactivated by H_2O), 30% (on a weight basis) sulfuric acid silica (5 g) and anhydrous sodium sulfate. The column was firstly pre-washed with 30 mL of dichloromethane/hexane (1:4) for the elimination of impurity coming from the silica gel. Then, the extracts were transferred to the top of column and the substances we interested were eluted by 50 mL dichloromethane/hexane (1:4). The fraction was evaporated by rotary evaporator and then reduced to 100 μL under gentle N_2 stream for further analysis.

The samples were analyzed on an Agilent 7890 series gas chromatograph (GC) equipped with a micro-cell electron capture detector (μ-ECD). The separation was performed on a fused silica capillary column (DB-5, 30 m × 0.318 mm i.d., and 0.25 μm film thickness). The carrier gas was nitrogen with a flow of 1 mL/min. The injector and detector temperatures were 230 and 300°C, respectively. The GC oven temperature program was carried out as follows: initial temperature 80°C held for 2 min, increased to 100°C at 5°C/min held 1 min, and then to 160°C at 10°C/min, to 260°C at 4°C/min, held for 10 min. Sample (1.0 μL) was injected in splitless mode. To confirm the results, selected typical samples were checked with an Agilent 6890 GC-5973 MSD system. The GC–MS parameters were the same as described above except that the carrier gas was helium. The mass spectrometer was operated in electron impact ionization mode with electron energy of 70 eV. Target compounds were monitored with selected ion monitoring (SIM) mode. This method could not separately quantify 1,2,3,5- and 1,2,4,5- congeners of TeCB, and therefore, they are quantified together as a compound (namely, TeCB2).

Field blanks consisted of pre-cleaned soil and pre-cleaned cotton which was taken to the sampling sites. Laboratory blanks were run to demonstrate freedom from interference and cross-contamination. In addition, a procedural blank was run in parallel for every set of six samples to check for interference and cross-contamination. The duplicate samples were analyzed in the laboratory along with regular samples, as another quality control tool to ensure the validity of the results. None of the target compounds were detected in the field blanks. Identifications of CBs were confirmed, and concentrations were measured using an external quantification standard consisting of known amounts of the target compounds. Two quality control criteria were used to ensure correct identification of the target compound: (1) The GC retention times matched those of the standard compounds within ± 0.05 min. (2) The signal-to-noise ratio was greater than 3:1. The limits of

detection (LOD) for CBs were defined by a signal-to-noise ratio greater than three times the average baseline variation. The residue concentrations in samples below detection limits were regarded as zero in the calculations of the sum and mean. The LODs for HCB, PeCB, 1,2,3,4-TeCB and TeCB2 (included 1,2,3,5- and 1,2,4,5- congeners of TeCB) were 0.04, 0.04, 0.1, 0.1 ng/g dry weight, respectively. The mean matrix spike recoveries of HCB, PeCB, 1,2,3,4-TeCB and TeCB2 were 86.5%, 82.0%, 77.6% and 75.1%, respectively. The recovery of the TCMX surrogate in all samples was in the range 70%–90%.

Results and Discussion

Only HCB was detected in all outdoor samples (Table 2). Except of CB-9, a city square dust sample, in which the percentage of HCB in ∑CBs (sum of 1,2,3,4-TeCB, TeCB2, PeCB and HCB) was 40%, the dominate part of the CBs residue in outdoor dust samples was HCB accounted for 55%–100% (in which the other compounds were not detected). The highest concentration was found in CB-15 which was collected from a metal industrial park. HCB in this sample was 51.61 ng/g dry weight and the ∑CBs was 52.63 ng/g dry weight. If the CB-15 was eliminated from industrial park samples, the HCB and ∑CBs mean concentrations of industrial park samples were only 1.41 and 1.78 ng/g dry weight, respectively. Compared with other studies, the median HCB concentrations in the present study were lower to the levels found in soil in Belgium, Italy, Greece, and Romania (Covaci et al. 2002), and close to that found in soils from Beijing, China (Zhou et al. 2007). The mean HCB concentration (4.13 ng/g dry weight) in this study was in the range of global background soil HCB levels (ranging from 0.010 to 5.20 ng/g dry weight with a mean of 0.680 ng/g dry weight) (Meijer et al., 2003). And the mean PeCB concentration was close to the soil from Estonia (Roots et al. 2010).

Principal component analysis (PCA) was performed to evaluate similarities or differences between the CB congener patterns of each samples, all data were normalized to a percent of the sum of CBs. PCs were determined by eigenvalues of over 1. As shown in Fig. 1a, two extracted PCs could explain 81.8% of the data variance. In the score plot of PCA (Fig. 1b), only three samples (CB-15 from a metal industrial park; CB-19 and CB-6 from two hospital), which had higher concentrations of HCB and PeCB, were scattered at the right of illustration. Most dust samples were assembled at the left of illustration, indicate the low CBs concentrations and the compositions of CBs in the most outdoor dust samples were similar, possibly originating from the similar source.

Photodechlorination and anaerobic biological dechlorination of HCB are not expected to lead to a net accumulation of PeCB in the environment and global emissions of PeCB around the year 2000 are clearly dominated by combustion sources. (Bailey 2007). Chlorobenzenes can be formed by waste incineration processes and from other thermal processes, e.g., in metal industry or biomass combustion. In these processes, PeCB (and TeCBs) are formed in higher concentrations compared to HCB (Weber et al. 2008). Industrial HCB was emitted in the 100,000-t scale in history (Barber et al. 2005) containing PeCB as an impurity and were distributed in the environment. Technical grade HCB contains about 98% HCB, 1.8% PeCB and 0.2%

Table 2 Chlorobenzene concentrations in outdoor dust samples

Sample style	Compound	Occurrence (%)	Range (ng/g dw)	Mean (ng/g dw)	Median (ng/g dw)
Park area	1,2,3,4-TeCB	50.0	ND–0.32	0.14	0.12
	TeCB2	50.0	ND–0.21	0.08	0.06
	PeCB	75.0	ND–0.47	0.16	0.10
	HCB	100.0	0.18–3.06	1.04	0.47
	∑CBs		0.34–3.98	1.43	0.56
Living area	1,2,3,4-TeCB	50.0	ND–0.32	0.12	0.09
	TeCB2	62.5	ND–0.62	0.24	0.15
	PeCB	75.0	ND–0.74	0.26	0.14
	HCB	100.0	0.71–5.26	2.12	1.41
	∑CBs		0.71–6.59	2.74	1.98
Industrial park	1,2,3,4-TeCB	37.5	ND–0.24	0.08	ND
	TeCB2	50.0	ND–0.49	0.14	0.08
	PeCB	87.5	ND–0.54	0.22	0.21
	HCB	100.0	0.13–51.61	7.69	1.39
	∑CBs		0.13–52.63	8.14	1.89

dw dry weight, *ND* not detected, *1,2,3,4-TeCB* 1,2,3,4-terachlorobenzene, *TeCB2* 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes, *PeCB* pentachlorobenzene, *HCB* hexachlorobenzene, ∑*CBs* sum of 1,2,3,4-TeCB, TeCB2, PeCB and HCB

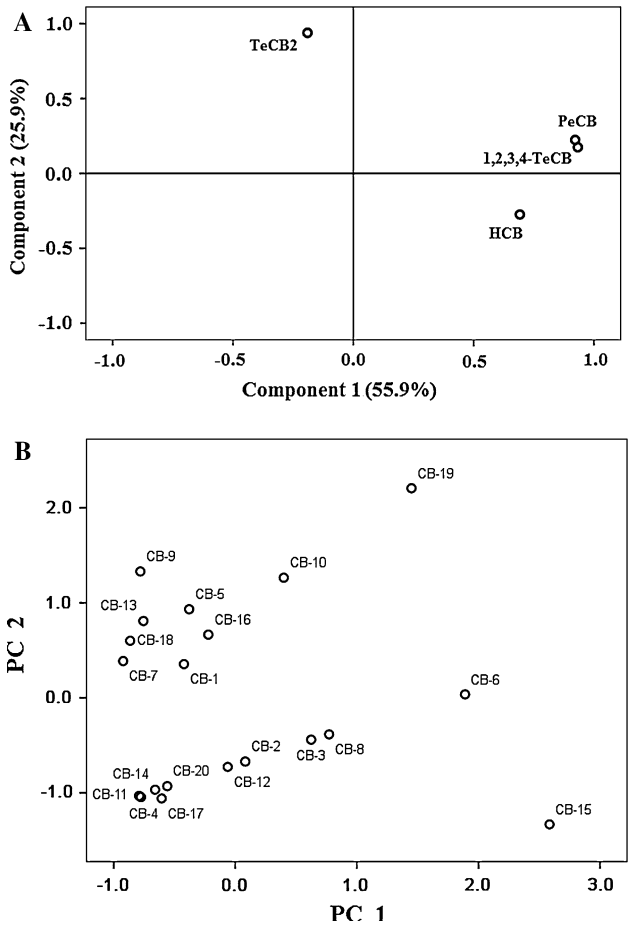

Fig. 1 Two-dimensional principal component loading plot (**a**) and score plot (**b**) obtained from the CB data of outdoor dust samples

1,2,4,5-TeCB (WHO-IPCS 1997). So, Roots et al. (2010) inferred that the HCB and PeCB residue in the soil of Estonia, which has a relatively consistent ratio of HCB/PeCB (ranging between 2.5 and 5.6), do not stem from incineration processes but mainly from the revolatilization of industrial HCB with a minor impact of PeCB. In the present study, PeCB was not detected in 4 of the 20 outdoor dust samples. The ratio of HCB/PeCB in most other dust samples were ranged from 2.9 to 7.9 (Fig. 2). Three dust samples (CB-1 from a habitation block, CB-15 from a metal industrial park and CB-17 from a power plant) had obviously higher ratio of HCB/PeCB. HCB has never been used directly as a pesticide in China, but other pesticides containing HCB are produced and used widely in China, for example, HCB concentration in picloram in China was 1.15 mg/kg and in chlorothalonil was 42.2 mg/kg in China (Wang et al. 2010). However, PeCB was identified in pentachloronitrobenzene (quintozene), endosulfan, chlorpyrifos-methyl, atrazine, and clopyrilid, but not in simazine, chlorothalonil, picloram and dacthal (USEPA 1998). The higher ratios of HCB/PeCB in the outdoor dust samples in

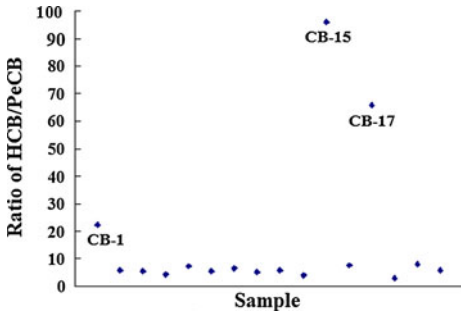

Fig. 2 HCB/PeCB in outdoor dust samples

the present study indicate that pesticide application may be an important source of HCB in the environment because of widespread use of pesticides and the lack of strict regulations on HCB impurity in pesticides in China.

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