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Polychlorinated Biphenyls Residues in the Soil in Linfen, China

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Abstract A total of 10 surface soil samples covering the whole territory of Linfen city were collected for analysis the 144 polychlorinated biphenyls (PCBs). The total PCBs concentration ranged from 0.2 to 3.4 ng g^{-1} in urban soil and 0.5 to 14.8 ng g^{-1} in industrial plant soil. Furthermore, increasing PCBs contamination was observed in northeast Linfen because of the distribution of industrial plants. Principal component analysis (PCA) revealed that the major source of PCBs in Linfen may be potentially associated with commercial #1 PCB through the long-range transmission. In total, PCBs were not a severe contamination in Linfen from current results.

Keywords China · Contamination · Linfen · Polychlorinated biphenyls · Soil

Polychlorinated biphenyls (PCBs), listed along with 11 other compounds as persistent organic pollutants (POPs) by the Stockholm Convention on May 22, 2001, are stable in the environment, are able to undergo long-range atmospheric transport, and possess the ability to bioaccumulate through the food chain (UNECE 1998). PCBs are a class of 209 congeners that were widely used in variety of electrical applications such as dielectric fluid in transformers and large capacitors, heat transfer fluids, hydraulic fluids, and so on. Thus, PCBs have been extensively studied with regard to their carcinogenic and mutagenic properties (WHO 2000). The research results published up to now have focused on central and western Europe, North America, and Japan. There is particularly a shortage of data from China and Russia (Meijer et al. 2003).

The city of Linfen is located in the southwest of Shanxi Province, China, an area of 20,275 km^2. The urban area is located mainly in the central part of Linfen, with 339,800 residents. The climate is dominated by temperate semi-wet monsoon, with a mean annual temperature of 12.2°C. China clay is the main representative soil type in Linfen, which is the heavy chemical industry base of China. With the development of industry in recent years, Linfen has provided increasing amounts of chemical products and secondary energy, such as coke and electric power. At the same time, environmental contamination has become more and more serious, but the levels of PCBs residues in the soil of Linfen have not been investigated in detail.

Due to the paucity of data on levels of PCBs in the soils of Linfen, this study investigated the composition, distribution, and characterization of PCBs in the soil samples obtained from urban areas and industrial plants of Linfen city, Shanxi province. The objectives were to determine the spatial distribution of these PCBs, to identify the possible sources of pollution, and to explore possible factors affecting contamination in order to prevent further environmental deterioration in Linfen.

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Materials and Methods

Surface soil samples (0–10 cm depth) were obtained from five urban sites and five industrial plants in Linfen, Shanxi Province (Fig. 1), in January 2006. Any overlying vegetation was removed before samples of the surface soil were collected in triplicate using a hand-held coring device. Each composite urban soil sample consisted of nine sub-samples in the same grid pattern at each sampling site. Each composite industrial plant soil sample consisted of three sub-samples. The gathered samples were freeze-dried, mixed thoroughly, sieved to 60 mesh (International standard size, 250 μm), transferred to amber glass and stored at 4°C. The remaining water content in the soil was determined gravimetrically after drying individual composite soil samples in air at 105°C for 12 h. All results are reported on a dry weight basis.

We purchased the standard solutions of PCB congeners from AccuStandard Inc. (New Haven, CT, USA). We diluted the five PCB calibration mixtures, which provided 144 congeners, with iso-octane to 20 ng mL^{-1} for each congener. Decachlorobiphenyl (CB-209) as a surrogate was purchased from Supelco (Bellfonte, PA, USA). Standard reference material (SRM) GBW08307 (reference soil for PCBs congeners analysis) was obtained from the National Research Center for Certified Reference Materials of China. All solvents used were of pesticide grade (J. T. Baker, Phillipsburg, NJ, USA).

Five grams of each soil sample was weighed then ground with anhydrous sodium sulfate into a free-flowing powder. The samples were extracted with 30 mL of hexane/dichloromethane (1:1, v/v) by ultrasonication for 4 min then separated by centrifugation. This process was repeated three times. Before extraction, 10 ng CB-209 was added as a surrogate standard. The concentrated extracts were reduced to a volume of 1 mL under a gentle stream of N_2.

The concentrated extracts were cleaned up using a chromatography column (20 cm × 15 mm i.d.) containing 2 g silver nitrate silica (10%, w/w), 1 g activated silica gel, 3 g basic silica gel, 1 g activated silica gel, 4 g acid silica gel (44% concentrated sulfuric acid, w/w), 4 g acid silica gel (22% concentrated sulfuric acid, w/w), 1 g activated silica gel, and 1 cm anhydrous sodium sulfate. The PCBs fraction was eluted with 100 mL hexane. The elution was evaporated with a rotary evaporator and then reduced to 50 μL under a gentle N_2 stream for analysis.

Analysis of PCBs was carried out with an Agilent 6890 series gas chromatograph coupled with an Agilent 5973 mass spectrometer (MS) using electron impact ionization (EI) source in the SIM mode. In EI mode, the MS source temperature was 230°C, and the electron energy was 70 eV. The GC was equipped with a split-splitless injector held constant at 270°C. Gas chromatographic separation was performed on a 30 m DB-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. The GC column was maintained at 75°C for 2 min then ramped at 15°C/min to 150°C, further ramped at 2.5°C/min to 280°C and held at this temperature for 15 min. The total run time was 64 min. Quantification of the samples was performed using an external standard method.

A laboratory method control group was run to demonstrate the lack of interference and cross-contamination. In addition, a procedural blank was run in parallel with every set of six samples to further check for interference and cross-contamination. Duplicate samples were analyzed in the laboratory along with the regular samples, as an additional quality control assessment to ensure valid results. Instrument stability and relative response factor variance

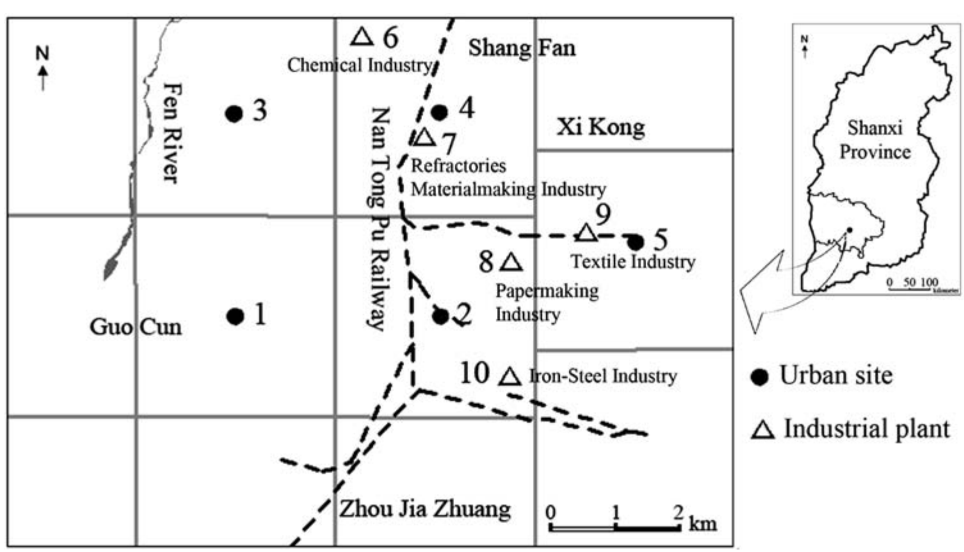

Fig. 1 Surface soil sampling sites in urban areas of Linfen

were determined by analyzing the calibration standard solutions in each sample batch.

Quantification of PCBs was performed using an external standard method. Three quality control criteria were used to ensure correct identification of the target compounds: (1) GC retention times matched those of the standard compounds within ±0.05 min; (2) the signal-to-noise ratio was greater than 3:1; (3) each compound had two monitored ions. Isotopic ratios between quantitative and confirmation ions were within ±15% of theoretical values. The limits of detection (LOD) for PCBs were defined by a signal-to-noise ratio greater than three times the average baseline variation, and were within the range of 0.01–0.05 ng g^{-1} (dry weight). The matrix spike recoveries of the 144 PCB congeners were within the range of 75–110%. The recovery of CB-209 surrogate in all samples was within the range of 75–115%. The results met the acceptance criteria specified in the US-EPA method 1668A (25–150%).

The SRM sample (GBW08307) was analyzed to validate the analytical method employed. The results were satisfactory with a z-score ≤1 for all congeners (range: 0.02–0.64 for the PCBs, $p < 0.05$). Recovery of CB-209 surrogate was 85% with the GBW08307 sample, which also met the acceptance criteria specified in the US-EPA method 1668A (25–150%).

Results and Discussion

About 144 PCBs were identified in all of the urban and industrial plant soil samples. The detection rates of PCBs in the soils were up to 100%, which indicate wide occurrence of these compounds in Linfen city. The total PCBs concentration (defined as the sum of 144 PCBs) ranged from 0.2 to 3.4 ng g^{-1} (median: 1.0 ng g^{-1}, dry weight) in urban soil and 0.5–14.8 ng g^{-1} (median: 2.4 ng g^{-1}, dry weight) in industrial plant soil (Fig. 2). The medians concentration in the soil of industrial plant was slight higher than those obtained in the soil of urban area.

We further compared the soil concentrations of PCBs reported elsewhere in literature. The median concentration in the present study were lower than that of the global background soil (5.4 ng g^{-1}, dry weight) (Meijer et al. 2003). In comparison with other areas of China, the levels were similar to those of the surface soil of Kunming and Shanghai, China (1.84 ng g^{-1} and 1.73 ng g^{-1}, dry weight, respectively) (Ren et al. 2007). In contrast to other countries, the levels were lower than those in Spain (4.4–4.8 ng g^{-1}) (Nadal et al. 2007), the levels were higher to those in the northeastern Sao Paulo, Brazil (0.02–0.25 ng g^{-1}) (Rissato et al. 2006), and were lower than those of surface soil of the Seine basin in France (0.09–150 ng g^{-1}) (Motelay-Massei et al. 2004). Compared to

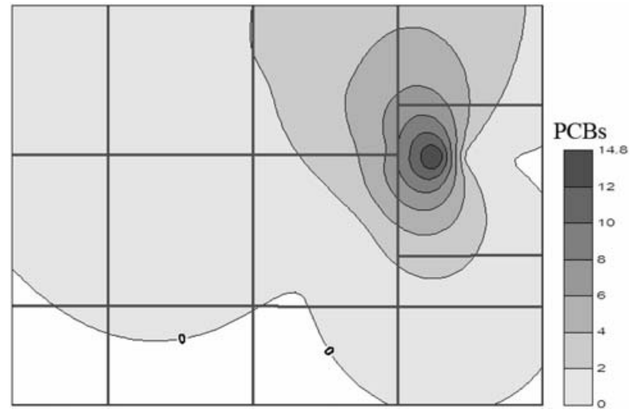

Fig. 2 The distributions of PCBs in the soils in Linfen (data in the Figure are in units of ng g^{-1})

the allowable level of 60 ng g^{-1} for PCBs in soil approved by the former Union of Soviet Socialist Republics (USSR) Ministry of Health in 1991, the contamination of soils in the present study had relatively slight PCB contamination levels on average (Bobovnikova et al. 1993; Bi et al. 2002).

The distribution of ΣPCBs in the soil samples shows in Fig. 2 revealing an increasing trend in the northeast Linfen. Possible reason was the distributions of industrial plants that was mainly built in the north and east area of Linfen. The contamination status of industrial plant soils about PCBs was higher than other urban area of Linfen. Such reason could possibly explain the climbing tendency of contamination status in northeast area of Linfen.

Of the PCB homologues, the dominant PCBs detected in this study were tri-CBs accounting for 45.7% of the total PCBs as a median. Higher-chlorinated congeners were detected at relatively low concentrations. The main PCB homologue in the average Chinese background and rural soils was tri-CBs (55 and 38%, respectively) (Ren et al. 2007). Furthermore, tri-CBs was also the major PCBs in the air samples of the Pearl River Delta (36.03–42.73%) (close to the City of Guangzhou, China) (Li et al. 2007). PCB homologue patterns in other countries were reported in the literature. The major PCB homologue was the tetra-PCB, and tri-PCB in the urban air samples in Europe (Howel 2007).

In China, approximately 10,000 tons of PCBs were produced in China from 1965 to 1974, with 9,000 tons as tri-chlorobiphenyl (#1 PCB) and 1,000 tons as penta-chlorobiphenyl (#2 PCB) (Xing et al. 2005). #1 PCB contained 42% chlorine, which was similar to Aroclor 1242, and #2 PCB contained 53% chlorine, similar to Aroclor 1254 (Jiang et al. 1997). The major homologue produced and used in China was tri-PCB, the major homologue profile of the global PCB product was also tri-PCB, and the composition of homologue was higher in

Chinese product than in global product (40.4 versus 25.2% for tri-PCB) (Breivik et al. 2002). Therefore, tri-CBs should be the dominant PCBs in the soil of Linfen.

Principal component analysis (PCA) progress was performed to evaluate similarities or differences between the PCB congener patterns of each sample; all data were normalized to percent of ΣPCBs. PCs were determined by an eigenvalue of over 1. By processing, two extracted PCs could explain 59.7% of the data variance. A loading plot and score plot rotation were obtained after varimax. Component 1 in Fig. 3 accounted for 31.2% of the total variance and was characterized most positively by penta-, hexa-CBs and was most negatively characterized by tri-CBs, while Component 2 accounted for 28.5% and was characterized by hepta-, nona-, octa-CBs. The score plot (Fig. 4) indicated that the compositions of PCBs in the soil samples were similar, possibly originating from the same source. The PCBs found in Linfen could therefore be classified into one main group relatively highly contaminated by tri-CBs. A clear clustering of samples was also observed, showing that tri-CBs are indeed the dominant contamination in the soil of Linfen. All these samples as well as commercial #1 PCB were characterized by a higher proportion of tri-CBs in the PCB profiles, which indicates that the sources of PCBs for these sampling locations may be potentially associated with commercial #1 PCB through the long-range transmission.

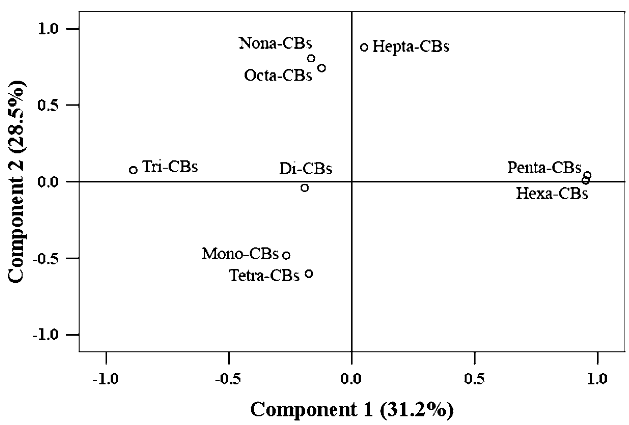

Fig. 3 Two-dimensional principal component loading plot obtained from the data correlation matrix of 10 soil samples in Linfen

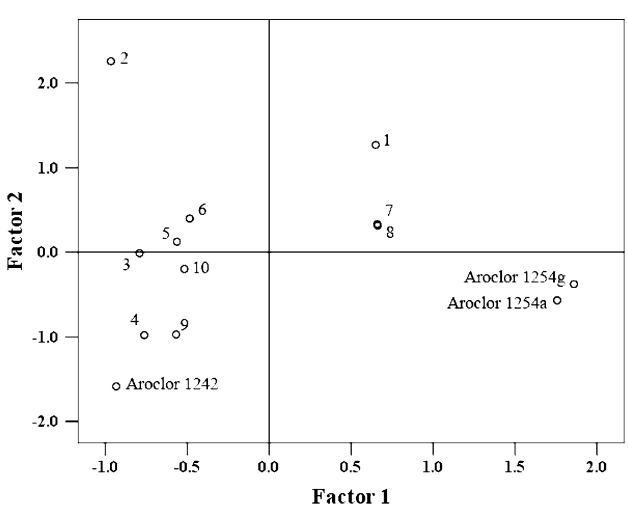

Fig. 4 Two-dimensional principal component score plot obtained from the data correlation matrix of 10 soil samples in Linfen

The present work investigated the compositions, distributions and characterization of PCBs in the soils from urban area in Linfen. Tri-CBs were the predominant congener (45.7% of the total PCBs as a median) in all samples. The results also indicated that the contamination status of the PCBs tended to increase in the northeast Linfen, possibly as a result of the distribution of industrial plants. Principal component analysis revealed that the major source of PCBs in Linfen may be potentially associated with commercial #1 PCB through the long-range transmission. Overall, PCBs were not a severe contamination in the soils of Linfen from current results. However, the results highlight that more attention should be paid to the industrial plants in such areas, since it is necessary to monitor the status of PCBs continuously.

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