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Topsoil dichlorodiphenyltrichloroethane and polychlorinated biphenyl concentrations and sources along an urban-rural gradient in the Yellow River Delta

Wenjun Xie[1], Aiping Chen[2], Jianyong Li[3], Qing Liu[1], Hongjun Yang[1], Tao Wu[1], Zhaohua Lu[1,2,*]

1. Shandong Key Laboratory of Eco-Environmental Science for the Yellow River Delta, Binzhou University, Binzhou 256603, China. E-mail: xwjeric@yahoo.com.cn
2. Institute of Restoration Ecology, China University of Mining and Technology, Beijing 100083, China
3. Jinan Entry-Exit Inspection and Quarantine Bureau, Jinan 250000, China

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Abstract

The Yellow River Delta (YRD) is a typical agricultural and petrochemical industrial area of China. To assess the current status of soil dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCB) residues, topsoil samples (0–15 cm) (n = 82) were collected in Bincheng District, at the geographic center of the YRD. The total concentrations of six DDT homologues were within 3.3–3819 μg/kg, with a mean concentration of 191 μg/kg, showing significant increase along urban-rural gradient. Soil concentrations of seven indicator PCBs in the area ranged from non-detectable to 87.0 μg/kg, dominated by heavily chlorinated PCBs (PCB-101 and -118). Soil PCBs concentrations were significantly greater in urban than suburban and rural areas. Principal component and multiple linear regression analysis suggest that 86.4% of soil DDTs originate from past DDT usage, and 13.6% originate from dicofol application. Soil PCBs most likely originate from the petrochemical industry (77.1%), municipal solid waste disposal (16.5%), local commercial PCB homologues usage (5.2%), and long-range atmospheric deposition (1.2%). In general, soil DDTs pollution was classified as low level, and mean PCBs concentrations were below the severe contamination classification range. Because PCB-118 is a dioxin-like congener, monitoring and remediation is advised to assess and reduce negative environmental and human health effects from soil DDTs and dioxin-like congeners in the study area.

Key words: DDTs; PCBs; Yellow River Delta; source apportionment; risk assessment
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Introduction

Soil is an important reservoir for many persistent organic pollutants (POPs) including dichlorodiphenyltrichloroethane and its metabolites (DDTs) and polychlorinated biphenyls (PCBs), which both have the potential to mobilize after volatilization from soil. DDT is a kind of organochlorine pesticide which was widely used for pest control in the past. By 1983, when the Chinese government banned the use of DDT for agricultural purposes, a total of 270,000 tons DDT had been produced in China (Zhang et al., 2002). Even after three decades, DDTs are still found widely in soils (Zhu et al., 2005; Zhang et al., 2006; Yang et al., 2009), and can potentially be taken up by crops and grazing animals, and eventually reach the human food chain (Bayat et al., 2011). They may also be mobilized by field run-off and reach the watershed or be emitted into the atmosphere through volatilization, which indirectly results in water and atmospheric contamination and impose serious threats to human health and the environment (Dai et al., 2011).

PCBs have been used worldwide in electrical applications such as capacitors, transformers, ship paint, and carbon-free copy papers (Breivik et al., 2002). Approximately 10,000 tons of PCBs were produced in China from 1965 until it was banned in 1974, with 9000 tons in the form of trichlorobiphenyl, similar to Aroclor 1242, and 1000 tons in the form of pentachlorobiphenyl, similar to 1254 (Jiang et al., 1997). Because they are semi-volatile and toxic to ecosystems and humans, PCBs are receiving intense scientific and regulatory attentions. Certain soils receive inputs of such chemicals at contaminated sites, however, at regional and global scales, most soils receive inputs of PCBs from local atmospheric deposition and long-range atmospheric transport (LRAT). Many surveys have measured PCBs concentrations in topsoil of China (Ren et al., 2007; Zhang et al., 2011). Results show that soil PCBs concentrations are higher in urban soils, and monitoring and remediation are advised, especially at

* Corresponding author. E-mail: lu-zhh@263.net

e-waste recycling sites (Bi et al., 2002; Wang et al., 2008).

The Yellow River Delta (YRD) lies in East China is a typical agricultural and petrochemical area. Soil DDT and PCB pollution in the region can be strongly influenced by agricultural and oil refinery production (Qiu et al., 2005; Kaisarevic et al., 2007). It is therefore necessary to evaluate the current status of DDT and PCB residues in the region. However, little is known about soil POPs contamination in the YRD. In this study, a survey of soil DDTs and PCBs concentrations were conducted in the Bincheng District, an area representative of the YRD. The objectives were to determine the residual levels, spatial distribution, and composition patterns of soil DDTs and PCBs in the district and identify their possible sources.

1 Materials and methods

1.1 Study area

Bincheng District is in Binzhou City, located at the center of the YRD, China, which covers about 1000 km^2. The gross outputs of agriculture and petrochemical industry account for roughly 10% and 30% of the total output, respectively. Soil in this area is derived from alluvial sediments of the Yellow River, and is classified as Aquic Inceptisols (Li, 2001).

1.2 Soil sampling and preparation

Topsoil samples (0–15 cm) (n = 82) were collected from rural, suburban, and urban areas in September, 2009, using a stainless steel shovel. Sample location coordinates were recorded with a handheld GPS receiver (Fig. 1). In the rural and suburban areas, samples were mainly collected from farmland and woodland, and in the urban areas, samples were collected from residential, commercial, and industrial land. Samples were put into solvent-rinsed brown glass bottles with a teflon cap, and stored frozen (–20°C) until analysis. Before extraction, soil samples were freeze-dried and sieved to less than 2 mm. Soil organic C and total N concentrations were 0.72%–2.05% and 0.06%–0.12%, respectively, and mean pH was 7.8.

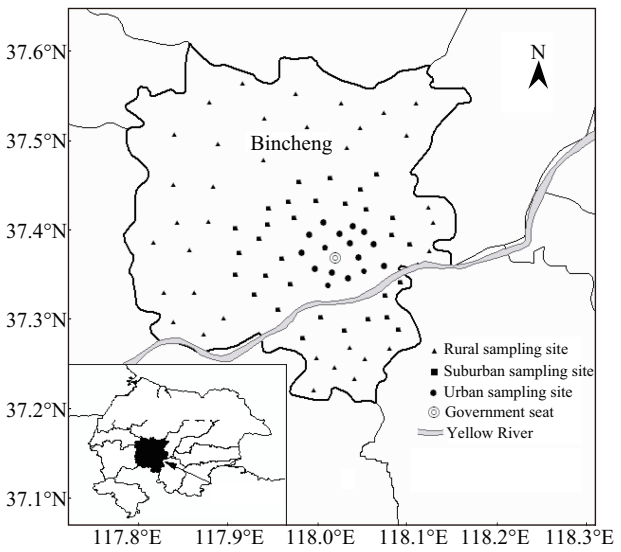

Fig. 1 Map of soil sampling sites for DDT and PCB analysis in Bincheng District.

1.3 Sample extraction and cleanup

Determination of DDT congeners (p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD) and PCB congeners (IUPAC no. 28, 52, 101, 118, 138, 153, and 180) was conducted based on the method of Ren et al. (2007) and Hoai et al. (2010). Briefly, soil samples were extracted with n-hexane/acetone (1:1, V/V) using a Speed Extractor (E-916, Büchi). A 10 g dry sample was mixed with 3 g of quartz sand and placed in a 20 mL extraction cell with a temperature and pressure of 100°C and 120 bars. After 2 cycles, the solvents were completely evaporated by vacuum and the extracts were taken up in 2 mL n-hexane, and then divided into two 1 mL fractions, which were used to determine DDTs and PCBs, respectively. Pigments, humic acids, etc. in two fractions were removed from the extracts by concentrated H_2SO_4 (98%). This step was repeated several times until the n-hexane layer became colorless. Further purifying was conducted using a chromatographic column filled with anhydrous sodium sulfate and activated silica gel. One fraction was eluted with n-hexane for PCBs analysis, the other was eluted with n-hexane/acetone (9:1, V/V) for DDTs analysis. The effluent of two fractions was concentrated to 1 mL using rotary evaporation.

1.4 DDT and PCB analysis

Using the splitless mode, a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) with helium as a carrier gas was applied for the separation of DDTs and PCBs on the GC system. The PCBs analysis was conducted with an Agilent 7890 GC-μECD (Zhang et al., 2011). The injector and detector temperature were set at 220 and 270°C, respectively. The oven temperature program was set at 120°C; 10°C/min, 200°C; 2°C/min, 230°C; 7°C/min, 270°C (5 min). The determination of DDTs was conducted with an Agilent 7890/5975 GC-EI-MS (Hoai et al., 2010). Mass spectrometer detection was based on the selected ion monitoring system (SIM). The oven temperature was 100°C; 25°C/min, 170°C; 4°C/min, 190°C; 10/min, 230°C; 2°C/min, 240°C (5 min). The injector and detector temperatures were set at 250 and 300°C, respectively. Peak areas were calculated using Agilent Chem-Station software, and quantification was conducted using an external calibration method. DDTs and PCBs concentrations in this study are based on dry soil mass.

1.5 Quality assurance and quality control

For every 10 samples, a laboratory blank and a duplicate sample were incorporated in the analytical procedure. The analysis of blanks did not reveal PCBs or DDTs contamination. Average recovery experiments were conducted by adding a standard PCBs or DDTs mixing solution into the soil. After mixture and drying overnight in darkness, PCBs or DDTs was extracted and analyzed as described above. Detection limits for the six DDT congeners ranged from

0.005 to 0.015 μg/kg, and for the seven PCB congeners from 0.02 to 0.10 μg/kg. The mean recovery for DDTs varied from 87.4% to 110.0%, and varied from 73.2% to 96.3% for PCBs. Relative standard deviations for each compound and differences among duplicate samples were all within 15%.

1.6 Statistical analysis

All statistical analysis was conducted using SPSS 11.0 for Windows. To detect significant differences for DDTs and PCBs concentrations among areas and land uses, ANOVA and Least Significant Difference (LSD) were calculated. All significant differences reported are $p \leqslant 0.05$. Principal component analysis (PCA) with multiple linear regression (MLR) analysis was used to identify the possible sources of DDTs and PCBs. In the case of samples with the concentrations below detectable limits, zero was set for calculations.

2 Results and discussion

2.1 Concentrations and composition of DDTs

Soil DDT concentrations and composition in Bincheng District are shown in Table 1. The detection frequencies for six DDT congeners were within 28.1%–98.8%. *p,p′*-DDE with the highest detection frequency was detected in 98.8% of soil samples, and *o,p′*-DDD with the least detection frequency was detected in 28.1% of soil samples. The total concentrations of DDTs ranged from 3.3 to 3819 μg/kg, with a mean concentration of 191 μg/kg, which was much higher than the reported value in soils of the Yangtze River Delta (35.3 μg/kg; Li, 2004) and Pearl River Delta (37.6 μg/kg; Fu et al., 2003). Residual levels of organochlorine pesticides are affected by application history and agricultural practices (Boul et al., 1994). Hence this difference reflected intensive agricultural activities and more DDT input in this area compared to the Yangtze River Delta and Pearl River Delta regions.

Along the urban-rural gradient, DDTs concentrations increased significantly (Fig. 2). DDTs concentrations in rural soil was about 5 times higher than in urban soil, which suggests that DDTs mainly originated from agricultural production in the study area. DDTs concentrations in rural farmland were significantly lower than in rural woodland, while the opposite trend was in the suburban area. The possible explanation was that woodland in suburban area mostly used for environmental greening, and in the rural was mostly orchard involved the relatively intensive pest control.

Among DDTs, the predominant compound was *p,p′*-DDE, which accounted for 82.7% of the total DDTs concentration, followed by *p,p′*-DDT with 5.5%, and the least was *p,p′*-DDD with 1.3% (Fig. 2). The composition pattern of DDTs varied among areas. Along an urban-rural gradient, the *o,p′*-DDTs (*o,p′*-DDT, *o,p′*-DDE, and *o,p′*-DDD) percentages declined significantly, from 38.3% to 4.3%. One possible explanation is that after the ban of DDT for agricultural production, chemicals containing *o,p′*-DDT, such as dicofol, contributed more to DDT pollution in urban and suburban areas than in rural areas. DDE and DDD are the two main products of DDT degradation. DDT degrades to DDE under aerobic conditions and reductively degrades to DDD under anaerobic conditions (Fellenberg, 2000). Due to the ratio sequence DDE: DDT (10.05) > DDD:DDT (0.38) > DDD:DDE (0.10), DDT to DDE was the main degradation route in topsoil of the study area. Statistical analysis revealed soil organic C and total N concentrations were not well correlated with DDTs concentrations in the urban, suburban, or rural areas.

2.2 Concentration and composition of PCBs

The seven indicator PCBs in this study are commonly measured in PCB analysis and their concentrations are often used for comparison (Yeo et al., 2004). In this study, the mean total concentration of indicator PCBs was 2.6 μg/kg, and the total indicator PCBs concentrations ranged from non-detectable to 87.0 μg/kg (Table 1). The total indicator PCBs concentrations were comparable to those in Hong Kong (2.5 μg/kg; Zhang et al., 2007) and Dalian

Table 1 Concentration metrics of six DDT homologues and seven indicator PCB congeners of Bincheng District topsoil (unit: μg/kg dry mass)

Compound	Mean	Median	Range	Std. Deviation
p, p′-DDT	10.6	3.0	n.d.–123	22.7
o, p′-DDT	5.6	1.1	n.d.–85.1	15.0
p, p′-DDE	158	27.8	n.d.–3597	490
o, p′-DDE	8.8	n.d.	n.d.–226	30.2
p, p′-DDD	2.5	0.4	n.d.–69.8	9.2
o, p′-DDD	5.4	n.d.	n.d.–242	30.9
∑DDT	191	38.9	3.3–3819	531
PCB-28	0.01	n.d.	n.d.–1.2	0.1
PCB-52	0.01	n.d.	n.d.–0.7	0.1
PCB-101	1.6	n.d.	n.d.–86.7	9.7
PCB-118	0.7	n.d.	n.d.–19.7	2.2
PCB-138	0.3	n.d.	n.d.–2.3	0.5
PCB-153	0.02	n.d.	n.d.–1.7	0.2
PCB-180	0.08	n.d.	n.d.–3.0	0.4
∑PCB	2.6	0.6	n.d.–87.0	10.0

n.d.: signifies concentrations below the detection limit.

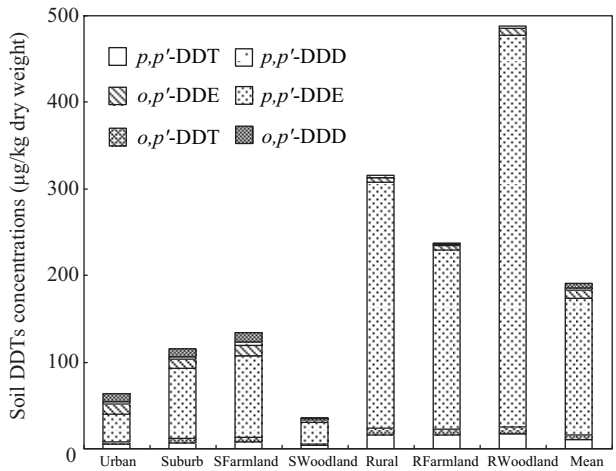

Fig. 2 DDT concentrations and compositions in topsoil from different areas and land-use in Bincheng District. SFarmland: farmland samples in the suburban area; SWoodland: woodland samples in the suburban area; RFarmland: farmland samples in the rural area; RWoodland: woodland samples in the rural area; Mean: mean values of total topsoil samples.

(2.8 μg/kg; Wang et al., 2008), but much lower than those in Yangtze River Delta (9.4 μg/kg; Zhang et al., 2011). The values were also lower than those in soils of industrial areas of Taiwan (94.9 μg/kg; Thao et al., 1993) and the Seine River Basin in France (73.9 μg/kg; Motelay-Massei et al., 2004). PCB-118 was detected in 47.6% of soil samples, the highest detection frequency of seven congeners, followed by PCB-138 (35.4%) (Fig. 3). The detected frequencies for other congeners were less than 10%. The dominant congener was PCB-101, accounting for 59.9% of total PCBs concentration, followed by PCB-118 which accounted for 25.6%. It was interesting that sampling sites with high PCB-101 detection frequencies and concentrations were usually near petrochemical and crude oil facilities. In this study, the PCB pattern was different from that in Hong Kong and the Yangtze River Delta, and the former was dominated by low chlorinated PCBs (⩽ tetra-CBs), and the latter was dominated by PCB-118 (Zhang et al., 2007, 2011). Therefore, the real patterns for PCB profiles vary among regions, which may be due to different industrial structures. Lower molecular PCB congeners (⩽ tri-CBs), which dominated rural areas in the national survey conducted by Ren et al. (2007), was not observed in this study. This is not surprising since the rural sites in our study are in closer proximity to urban areas than most rural sites in the national study (Wang et al., 2008).

Mean total concentrations of indicator PCBs in urban soils were much higher than in suburban and rural areas (Fig. 3). The proportions of PCB-180 and -101 were significantly higher in urban than in rural and suburban areas, while PCB-118 and -138 were significantly lower than in rural and suburban areas, especially in suburban soil with the highest percentage of PCB-118. PCB-118 is a mono-ortho PCB with a dioxin-like structure and is one of 12 WHO-specified PCB congeners that exhibited mutagenic activities (Shen et al., 2009). Zhang et al. (2007) assumed that this compound might originate from landfill/waste composting sites, which are usually located in suburban or rural areas. Pentachlorobiphenyl, known as #2 PCB, is similar to Aroclor 1254 and contains high proportions of PCB-118 and -138. Therefore, PCB contamination in suburban and rural soils might also be connected with commercial use of pentachlorobiphenyl. However, this needs further investigation to be verifiable.

Soil PCBs concentrations were higher in woodland soil than in farmland soil, especially in the rural area (reached the significant level). PCB-118 was the dominant congener in farmland, while PCB-101 was the dominant congener in woodland. The dominant congener of PCB-118 might result from the wastes application during farmland management. No correlation was also observed between PCBs concentrations and soil organic C and total N concentrations.

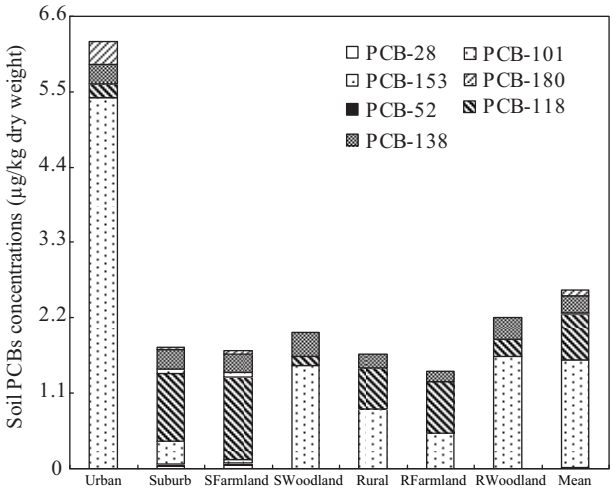

Fig. 3 PCB concentrations and compositions in soils from different areas and land-use in Bincheng District.

2.3 Sources of DDTs and PCBs in soils

Spatial distribution of DDTs in Bincheng District reflected historical agricultural usage in different areas. In general, a small *p*,*p*′-DDT/(*p*,*p*′-DDE + *p*,*p*′-DDD) ratio is indicative of aged (microbial degraded) DDT, and a value much greater than one indicates fresh application. In this study, *p*,*p*′-DDT/(*p*,*p*′-DDE + *p*,*p*′-DDD) ratios varied among soils from different areas and land-use, but all averaged less than one (Table 2). This shows that DDT residues in the study area were mainly from historical application. The ratios of *p*,*p*′-DDT / (*p*,*p*′-DDE + *p*,*p*′-DDD) in rural farmland were significantly greater than in other areas, indicating longer DDT usage history in rural farmlands. Ratios were higher than one for two sampling sites in rural farmland, showing possible illegal DDT usage (Yang et al., 2009). DDT containing dicofol usage is the other important source of DDTs entering soil, and DDTs from technical DDT can be distinguished from dicofol by the *o*,*p*′-DDT/*p*,*p*′-DDT ratio (Qiu et al., 2005). In this study, the *o*,*p*′-DDT/*p*,*p*′-DDT ratios among different areas and

Table 2 Ratios of DDT homologues of Bincheng District soils from different areas and land-use

Ratio		Urban	Suburb			Rural			T-total[a]
			Total	Farmland	Woodland	Total	Farmland	Woodland	
DDT/	Mean	0.15	0.12	0.12	0.13	0.44	0.61	0.07	0.26
(*p*,*p*′-DDE+*p*,*p*′-DDD)	Median	0.12	0.11	0.11	0.11	0.06	0.08	0.05	0.09
	Range	0.04–0.42	0.02–0.33	0.02–0.33	0.04–0.26	0–10.57	0–10.57	0–0.20	0–10.57
	> 1[b]	0	0	0	0	2	2	0	2
o,*p*′-DDT /	Mean	0.26	0.96	1.06	0.54	0.33	0.31	0.39	0.56
p,*p*′-DDT	Median	0.18	0.35	0.30	0.39	0.32	0.32	0.26	0.28
	Range	0–1.65	0–7.05	0–7.05	0–1.42	0–0.87	0–0.82	0–0.87	0–7.05
	> 1.3[c]	1	7	6	1	0	0	0	8

[a] Total topsoil samples in this study; [b] the number of topsoil samples with a ratio greater than 1; [c] the number of topsoil samples with a ratio greater than 1.3.

land-uses ranged from 0.26–0.96. The values in the rural and suburban areas were higher than in technical DDT (0.2–0.3) and lower than in dicofol (1.3–9.3 or higher). *o*,*p*′-DDT is less stable than *p*,*p*′-DDT in the environment (MacGregor, 1976), which resulted in lower observed ratios than those of the product formulas. Therefore, we can conclude that the release of dicofol contributed to soil DDT contamination in the study area. More dicofol was applied in the suburban farmland, as evidenced by their significantly higher ratios of *o*,*p*′-DDT/*p*,*p*′-DDT.

PCA and MLR are increasingly used to identify sources of organic pollutants in the environment (Li et al., 2006). The factor analysis conducted for six DDTs showed that the first two factors accounted for 95.0% of the total variance in the data set (Table 3). Factor 1 explained 67.9% of the total variance, which was highly dominated by *o*,*p*′-DDE, *o*,*p*′-DDD, and *p*,*p*′-DDD, and moderately included *o*,*p*′-DDT. *o*,*p*′-DDE and *o*,*p*′-DDD are metabolites of *o*,*p*′-DDT, which is considered to be the main impure compound in dicofol. A source of *p*,*p*′-DDD is the conversion of *p*,*p*′-Cl-DDT which is another major compound in dicofol (Qiu et al., 2005). Therefore, Factor 1 was mostly related to dicofol usage. Factor 2, which accounted for 27.1% of the total variance, was highly dominated by *p*,*p*′-DDT and *p*,*p*′-DDE, and moderately included *o*,*p*′-DDT. *o*,*p*′-DDT is an isomer in technical DDT and *p*,*p*′-DDE is a metabolite of *p*,*p*′-DDT. Therefore, this factor may be related to DDT residues from historical pesticide application. Individual contribution of different sources to the total DDTs in soils was obtained by the following MLR (Eq. (1)):

$$Y = 0.147X_1 + 0.93X_2 \quad (1)$$

where, Y (μg/kg) is the total soil DDTs concentration and X_1 and X_2 (μg/kg) are the DDTs entering soils from dicofol application and historical technical DDT application, respectively. In the study area, technical DDT usage contributed 86.4% of total DDTs in soils, dicofol application contributed 13.6%.

Factors 1, 2, 3, and 4 from factor analysis for PCBs explain 28.8%, 22.3%, 14.8%, and 14.2% of the total variance, respectively (Table 3). Factor 1 was highly dominated by two low chlorinated PCBs, PCB-28 and -52. Due to their low concentrations, high volatility and migration, Factor 1 was considered to be from long-range atmospheric deposition. This is in accordance with the industrial structure of the area, which involved little electrical production containing trichlorobiphenyl (high proportions of low chlorinated PCBs).

High chlorinated PCBs, PCB-138, -153, and -180 (⩾ Penta-CBs) formed a close group in Factor 2. This PCB profile pattern is related to pentachlorobiphenyl, which was another PCB product commonly used in China. Since high chlorinated PCBs are less volatile and more persistent in soil compared with low chlorinated congeners, Factor 2 is most likely related to local PCB homologues usage.

Factor 3 was dominated by PCB-118, which was found to be the dominant atmospheric compound near landfill/waste composting sites (Lua et al., 2003). Therefore, this compound was assumed to originate from municipal solid waste disposal (Zhang et al., 2007).

Factor 4 was dominated by PCB-101. The sampling sites with high PCB-101 detection ratios and concentrations were close to oil and petroleum facilities. The petrochemical industry is associated with soil PCB-101 concentrations (Kaisarevic et al., 2007). Accordingly, this factor might be related to the local petrochemical industry. Individual contribution of different sources to the total PCBs in soils was obtained by MLR (Eq. (2)):

$$Y = 0.015X_1 + 0.065X_2 + 0.208X_3 + 0.917X_4 \quad (2)$$

where Y (μg/kg) is the total soil PCBs concentration; and X_1 (μg/kg), X_2 (μg/kg), X_3 (μg/kg), and X_4 (μg/kg) are soil PCBs from long-range atmospheric deposition, local commercial PCB homologues usage, municipal solid waste disposal, and petrochemical industry, respectively. From Eq. (2) we deduced that atmospheric deposition, local commercial PCB homologue usage, municipal solid waste disposal, and petrochemical industry contributed to 1.2%, 5.2%, 16.5%, and 77.1% of soil PCBs residues, respectively.

2.4 Evaluation of DDT and PCB contamination in soils

According to the guidelines of the Chinese Environmental Quality Standard for Soils (GB15618-1995), soil can be classified as no DDTs pollution (< 50 μg/kg), low DDTs pollution (50–500 μg/kg), moderate DDTs pollution (500–1000 μg/kg), and severe DDTs pollution (< 1000 μg/kg). Mean total DDTs concentration was significantly higher than the maximum allowable concentration for no pollution soil, and significantly lower than the maximum allowable concentration of low pollution soil. Therefore, DDT pollution in most soils in the study area was classifies as low pollution soils. Soil concentrations in eight samples (five samples from the rural area, two samples from the suburban area and one sample from urban area) reached the

Table 3 Factor pattern for DDTs and PCBs in topsoil of Bincheng District

DDTs	Factor 1	Factor 2	PCBs	Factor 1	Factor 2	Factor 3	Factor 4
p, p′-DDT	0.24	**0.94**[a]	PCB-28	**0.99**	–0.02	–0.01	–0.00
o, p′-DDT	0.69	0.69	PCB-52	**0.99**	–0.02	–0.01	–0.00
p, p′-DDE	–0.01	**0.93**	PCB-101	0.01	–0.02	–0.01	**0.99**
o, p′-DDE	**0.98**	0.15	PCB-118	–0.02	0.01	**0.97**	–0.01
p, p′-DDD	**0.95**	0.31	PCB-138	–0.06	**0.69**	–0.16	0.05
o, p′-DDD	**0.99**	–0.01	PCB-153	0.02	**0.75**	0.30	0.00
			PCB-180	0.00	**0.71**	–0.02	–0.07
Loading (%)	67.9	27.1	Loading (%)	28.8	22.3	14.8	14.2

[a] Values with bold font represent high loadings in each factor.

moderate pollution level, and three samples (two samples from the rural area and one sample from the suburban area) had severe pollution. The DDT pollution levels in the rural area were significantly higher than in suburban and urban areas. Furthermore, Dutch soil guidelines and Canadian soil quality guidelines were also adopted to assess soil quality. The mean soil DDTs concentration in the study area was far higher than the target value (10 μg/kg) and lower than the intervention value (4000 μg/kg) in Dutch soil guidelines (VROM, 2000). According to Canadian soil quality guidelines for the protection of environment and human health, total DDTs concentrations of all soil samples in urban area were lower than the soil guideline value of 700 μg/kg for residential and parkland soils, and total DDTs concentrations in 8.6% and 6.5% of soil samples from rural and suburban areas were higher than the soil guideline value of 700 μg/kg for agricultural soils, respectively (CCME, 2007). Monitoring and remediation measures are advised in this area because ecology and human health are affected by these substances through the food chain at even relatively low concentrations (Wong et al., 2002).

Since, at present, no threshold values for PCBs in Chinese soil have been defined, Dutch soil guidelines and Canadian soil quality guidelines were used. Compared with the target value of 20 μg/kg for the sum of six PCBs (PCB-28, -52, -101, -138, -153 and -180) in Dutch soil guidelines (VROM, 2000), 98.9% of soil samples in Bincheng District met the Dutch standard for these congeners. Soil PCBs concentrations in the study area were much lower than the values of PCBs for agricultural (500 μg/kg) and residential and parkland soils (1300 μg/kg) in Canadian soil quality guidelines (CCME, 2007). PCB-118, dioxin-like congener, had the mean toxicity equivalent concentration of 0.02×10^{-3} μg/kg, which was much lower than the intervention value (0.18 μg/kg) in Dutch soil guidelines (VROM, 2000), while higher than that in Beijing, Harbin and Taiyuan (Wu et al., 2011). Accordingly, we conclude that topsoil in Bincheng District was not severely contaminated with PCBs. But, even so, regular monitoring and risk assessment for ecological and human health demands further attention, particularly in areas with high dioxin-like PCBs concentrations.

3 Conclusions

Mean topsoil DDTs concentrations were classified as low pollution, and PCBs were not severely contaminated in the study area. Soil total DDTs concentrations significantly increased along an urban-rural gradient, mostly due to the enhancement of agricultural activities, dominated by *p*,*p*′-DDE. In contrast, the higher concentrations of indicator PCBs were in urban soils, and PCB patterns were dominated by heavier chlorinated congeners in general (⩾ Penta-CBs). Based on PCA and MLR analysis, technical DDT application contributed 86.4% of total DDTs in soils, and dicofol application contributed 13.6%. PCBs in the study area most likely mainly originate from the local petrochemical industry (77.1%) and municipal solid waste disposal (16.5%). Since the dioxin-like PCB congener PCB-118 had high detection frequency and concentration, monitoring and remediation measures should be conducted to assess and reduce impacts to environmental and human health from soil DDTs and dioxin-like PCB congeners in the study area.

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