Movement and retention of polychlorinated biphenyls in a paddy field of WenTai area in China

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Abstract

Polychlorinated biphenyls (PCBs) are classified as priority pollutants by environmental agencies. A field investigation on polychlorinated biphenyls movement and retention in paddy field was conducted during 1993, 1997 and 1999 at the WenTai area. Soil, air and rice samples were analyzed. PCB concentrations in the soil showed a reducing trend with respect to time and depth. Most of the di-, tri-, and tetra-chlorinated PCB congeners showed significant decreases during the period, while the more highly chlorinated PCBs were more persistent in soil. The results of field investigation data showed that even though 6 years the PCB concentrations in two fields were far from reaching uniform. In addition, rice grown in the field appeared somewhat contamination by PCBs, but it was not likely subjected to concentrating PCBs from contaminated soil significantly. It was shown that the PCB concentrations in rice samples were not directly proportional to their concentrations in soil. Principal component analysis was performed with the standardized relative abundance of PCBs in the samples. All these observations indicated that the pattern of PCBs in soil cannot be considered to reflect the original pollution source. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polychlorinated biphenyls (PCBs) have attained considerable notoriety as ubiquitous environmental contaminants (WHO, 1993). Despite that their industrial use in many industrialized countries has been restricted since the 1970s. The subsequent disposal or dumping in landfills of PCBs has resulted in universal contamination of air, water and soil, etc. (Iwata et al., 1994). They have been included in the “priority pollutants” listings implemented by the US Environmental Protection Agency (USEPA) and by the Euro-

pean Commission. These compounds have also been considered for inclusion in the priority pollutant list of the State Environmental Protection Administration (SEPA) in China.

The chemical formula of PCBs can be presented as $C_{12}H_{10-n}Cl_n$, where n is the number of chlorine atoms within the range of 1–10. Theoretically, 209 congeners are possible, but only about 130 congeners are likely to be found in commercial products. All congeners of PCBs are low volatile and highly lipophilic, with the consequence that more than 99% of the environmental PCBs mass are found in soil. As organic pollutants, the most important aspects of the environmental behaviors of PCBs in soil are their disappearance rate by various mechanism, translocation from soil into plant tissues, and accumulation in the food

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chain. Marked dissimilarities in the rate and extent of PCBs sequestration are found in different types of soil (Chung and Alexander, 1998). It is generally agreed that human diet represents the main route of human exposure to PCBs. Because of their ability to biomagnify through the food chain and our relative topmost position in the food chain, the occurrence of PCBs in various types of food has been widely studied. Dietary intake with meal, fish and milk has been identified as the principal route of human exposure to PCBs (Jan and Adamic, 1991; Kannan et al., 1994; Ocker and Eich, 1992; Schecter et al., 1997; Theelen et al., 1993). However, The plant is the first link in the food chain.

Knowledge of the behavior of polychlorinated biphenyl congeners in natural flora and crop species is essential in elucidating their bioaccumulation in the food chain. There are only few studies of PCBs uptake by terrestrial plants, and they were mainly conducted under simulated conditions in growth chambers or green-house with spiked compounds (Webber et al., 1994). At present, it is suggested that the pathway of PCBs accumulation in plants might include: root uptake and transport to the shoot; contamination of shoots by soil particles and atmospheric deposition. Laboratory studies indicating uptake and translocation of PCBs via the root systems of plant have been reported by some workers (Suzuki et al., 1977). However, conflicting evidence suggests that PCBs uptake and transfer by crops is probably not a real transfer via the root system but only a partitioning process (Offenbaecher, 1992). There are major differences on the accumulation and transport behavior of PCBs by specific plants. Some terrestrial plants such as purple loosestrife (*Lythrum salicaria*), may accumulate PCBs via the root system (Bush et al., 1986). Other species, such as beans (*Phaseolus* spp.), may show no consistent increase over time (Bacci and Gaggi, 1985), while corn (*Zea mays* L.) even reduced their PCBs burdens over time (Shane and Bush, 1989). Some experiments reported that the atmospheric deposition was of far greater important pathway than soil–plant transfer for the accumulation of PCBs in plant (Muller et al., 1993).

Rice (*Oryza sativa*) is the predominant crop grown in south of China. As more than half of cropland in the area is paddy field, the movement and retention of PCBs under a paddy field system is an important concern. Not only is rice the main food of humans, but

also it is used widely as a livestock feed. An estimate of the amount of PCBs present in various ecological systems is important for the contaminated area and the remediation process. The aim of this work was to investigate the PCB concentrations in a system in the WenTai area. The movement and retention of PCBs in the system and the possible pathway of PCBs accumulation in rice were investigated.

2. Materials and methods

2.1. Sample collection

Samples were collected from a contaminated paddy field in WenTai area, located at 28°N, 120°45'E, in Zhejiang Province of China (Table 1). The soil was classified as Udic Ferrisols. In 1989, some arbitrary disposal of used electric appliances resulted in the PCBs pollution accident. There was no other PCBs pollution source near this area, so it offered an ideal place to study the movement of PCBs in the environmental system.

Soil and rice samples were collected in 1993, 1997 and 1999. Air samples (including the vapor and particulate) were collected in 1999. Soil samples were taken from a paddy field (Sites A and B) in which Site A was about 100 m long and 30 m wide the pollution point, and Site B bordered on Site A but was 100 m from the pollution point. The surface soil samples were (depth of 0–10 cm) taken at intervals while walking a “W” pattern over the croplands. In order to investigate the leaching behavior of PCBs in the field, 12 samples were collected at six depths (0–5, 5–10, 10–15, 15–20, 20–30, and 30–50 cm below surface) from two non-croplands at Sites A and B. All the soil samples were air-dried, ground and sieved to pass a 80 mesh, stored in sealed glass containers, and frozen in refrigerator until analysis. The rice was sampled from the same field as the soil samples, and all the samples including different tissues such as grain, stalk, husk and leaves were stored in refrigerator until analysis.

Particulate and vapor samples were taken simultaneously using a medium-volume (120 l/min) and low-volume air samplers (0.5 l/min) equipped with a filter and glass wool followed by a absorption tube containing 10 ml *N,N*-dimethylformamide to collect

Table 1

Sampling location, date and characteristics for study in the paddy field, WenTai area

Sample	Sampling medium	Sample location ^a	Characteristic	Depth (cm)	Date
S1	Soil	Site A	Cropland	0–10	1993
G1	Grain of rice	Sites A and B	Cropland		1993
T1	Stalk or rice	Sites A and B	Cropland		1993
H1	Husk of rice	Sites A and B	Cropland		1993
L1	Leaves of rice	Sites A and B	Cropland		1993
S3	Soil	Site A	Cropland	0–10	1997
S4	Soil	Site B	Cropland	0–10	1997
G2	Grain of rice	Sites A and B	Cropland		1997
H2	Husk of rice	Sites A and B	Cropland		1997
S5	Soil	Site A	Cropland	0–10	1999
S6	Soil	Site B	Cropland	0–10	1999
G3	Grain of rice	Sites A and B	Cropland		1999
T3	Stalk of rice	Sites A and B	Cropland		1999
H3	Husk of rice	Sites A and B	Cropland		1999
L3	Leaves of rice	Sites A and B	Cropland		1999
S7	Soil	Site A	Non-cropland	0–5	1999
S8	Soil	Site A	Non-cropland	5–10	1999
S9	Soil	Site A	Non-cropland	10–15	1999
S10	Soil	Site A	Non-cropland	15–20	1999
S11	Soil	Site A	Non-cropland	20–30	1999
S12	Soil	Site A	Non-cropland	30–50	1999
S13	Soil	Site B	Non-cropland	0–5	1999
S14	Soil	Site B	Non-cropland	5–10	1999
S15	Soil	Site B	Non-cropland	10–15	1999
S16	Soil	Site B	Non-cropland	15–20	1999
S17	Soil	Site B	Non-cropland	20–30	1999
S18	Soil	Site B	Non-cropland	30–50	1999
A1	Gaseous		Rural area		1999
A2	Gaseous		Rural area		1999
A3	Gaseous		Residential		1999
P1	Particle		Rural area		1999
P2	Particle		Rural area		1999
P3	Particle		Residential area		1999

^a Sampling location Site A: nearby the pollution source, Site B: bordered on Site A, but was 100 m from the pollution point.

particle- and gas-phase PCBs, respectively (Jing et al., 1992).

2.2. Extraction

Analytical procedure for PCBs in soil was described in detail elsewhere (Chu et al., 1996) and briefly described here.

Before the extraction, surrogate containing 3,5-dichlorobiphenyl (International Union of Pure and Applied Chemistry (IUPAC) no. 14) and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (IUPAC no. 209) was added to the samples.

For determination of PCBs in soil and rice samples, about 5–10 g finely ground sub-sample was homogenized with anhydrous sodium sulfate (Na_2SO_4) until free flowing powder was obtained. The sample was then extracted with 3×20 ml hexane/acetone (1/1, v/v) by ultrasonication and separated by centrifuging, then the extract was concentrated in Kudema–Danish (KD) apparatus to about 3 ml for further purification.

For determination of PCBs in the particulate-phase, the filters was Soxhlet extracted for 24 h with 100 ml hexane/acetone (1/1, v/v). The extract was concentrated, and the solvent was exchanged to hexane. For determination of PCBs in gas-phase, the

sampling solution of *N,N*-dimethylformamide was transferred to a separatory funnel with another 5 ml *N,N*-dimethylformamide, then 50 ml 3% Na₂SO₄ aqueous solution and 10 ml hexane was added to the funnel. After mixing and separation, the lower layer was discarded and the upper organic phase was extracted three times by the same procedure. The extract was dried with anhydrous Na₂SO₄ and then concentrated to 0.2 ml for gas chromatographic analysis.

2.3. Clean-up of PCB congeners

To clean-up the samples, concentrated sulfuric acid (volume 2 ml) was vigorously shaken with the extract in a test tube to eliminate interfering co-extractants and macromolecules. After centrifugation the acid phase was discarded. The procedure was repeated several times until the acid phase remained colorless. The extract was then washed with 2% NaCl aqueous solution, dried with anhydrous Na₂SO₄ and concentrated to about 1 ml.

For the soil and rice samples, fractionation was done with alumina–silver nitrate modified silica gel chromatography column. After the sample was transferred onto the column, PCB was eluted from the column with hexane in the first 150 ml fraction. The fraction was concentrated by KD apparatus and under a gentle stream of nitrogen to 0.5 ml.

For the determination of PCBs in particulate-phase, the interfering compounds were removed by eluting the extracts through a silica gel column with hexane. The extracts were further concentrated to 0.5 ml.

2.4. Determination of PCB congeners

Congener-specific PCBs analysis was performed on a Varian 3740A gas chromatograph equipped with ⁶³Ni electron capture detector and SE-54 column (0.25 mm × 40 m). The carrier gas was nitrogen. The injector and detector temperature were 300 and 350 °C, respectively. The oven temperature program was as follows: 50 °C hold for 2.0 min, then 4 °C/min, to 280 °C, hold 20 min. A 1 µl solution was injected with splitless mode. Data on the chromatogram from GC were collected with a WDL-95 workstation (Dalian Inst. Chem. Phys., China). Aroclor mixture was used for congener identification and quantification (Capel et al., 1985). The identifications were con-

firmed by HP 6890 gas chromatograph coupled to a HP 5973 mass spectrometer with select ion mode (SIM).

The PCB concentrations were quantified in comparison with the corresponding external standard calibration solution. Calibration curves were determined by diluting a stock solution and run daily. The following congeners were routinely analyzed in all samples: IUPAC no. 8, 19, 18/17, 16/32, 26/25, 31/28, 33, 22, 45, 46, 52, 49, 48/47, 44, 37/42, 41/64, 40, 74, 70, 66, 60/56, 101, 99, 83, 97, 87, 85, 110, 82, 118/108, 151, 146, 153, 141, 137, 138, 128, 178, 175, 187/159, 185, 174, 177, 172, 180, and 170. The $\sum$ PCBs referred in this study is the sum of these congeners. Residual water was measured by heating sub-samples in oven at 105 °C for 24 h and the results were expressed on a dry weight basis.

2.5. Quality control and quality assurance

The detection limit of PCBs in samples was designed to be three time of the values of procedural blanks. The average recoveries for PCBs through the analytical procedures (laboratory treatment) was 78% as determined by spiking 2 µg of Aroclor 1254 in the soil samples, and averaged the recoveries of Aroclor 1254. The recoveries of surrogates in all samples were 61.2–119% for PCB14 and PCB209, and the standard derivation was 14%.

3. Results and discussion

3.1. The PCBs concentration and congener distribution in soil samples

Soil samples collected from the pollution point were analyzed for PCBs and the results are given in Table 2. The PCB concentrations ($\sum$ PCBs) in soils for Site A ranged from 1100 ng/g in 1993 to 927 ng/g in 1999, which were significantly higher than those in sediments from Baiyangdian Lake and the Second Songhua River in China (Li et al., 1989; Zhu et al., 1995). Although the higher PCB concentrations in the rice field were much higher than the allowable level of 60 ng/g approved by the former USSR Ministry of Health in 1991, they were lower than those in some heavily contaminated area of other countries (Bobovnikova et al., 1993).

Table 2
Concentrations of PCB congeners in soil and rice samples (ng/g DW) from the paddy field, WenTai area

IUPAC no. ^a	S1 ^b	S3	S4	S5	S6
8	0.85	ND ^c	ND	0.50	0.75
19	9.70	ND	ND	ND	ND
18/17	110.6	ND	ND	13.45	0.27
16/32	32.1	0.32	1.08	2.33	0.14
26/25	31.4	6.84	7.30	5.16	0.19
31/28	102.1	79.89	57.00	51.09	10.16
33	36.4	6.52	5.11	3.16	2.89
22	17.9	0.96	ND	0.42	0.47
45	12.8	ND	ND	1.86	ND
52	73.0	82.76	32.96	19.06	8.38
49	47.5	18.09	18.93	10.56	5.66
47/48	37.7	18.20	13.93	12.80	4.08
44	58.4	63.33	50.35	18.12	6.15
37/42	36.2	ND	ND	10.64	5.27
41/64	65.0	44.58	26.24	20.40	6.83
40	10.0	0.80	0.54	1.94	0.28
74	46.5	33.06	20.03	16.79	5.81
70	56.3	35.98	27.01	14.09	6.33
66	72.5	62.19	40.38	26.08	8.62
60/56	37.9	16.97	10.16	12.22	0.20
101	28.8	56.70	29.74	93.11	25.33
99	16.3	34.88	17.21	61.28	15.26
83	1.7	7.38	3.64	ND	ND
97	9.4	26.44	13.29	48.80	13.06
87	ND	25.34	46.58	88.37	9.24
85	63.8	20.23	ND	ND	9.09
110	26.9	65.22	33.93	96.08	29.52
82	5.9	18.57	9.21	35.88	5.36
118/108	17.9	64.85	35.44	94.48	26.51
146	4.7	19.91	10.48	28.27	6.14
153	5.6	21.70	11.74	29.03	17.34
141	0.92	ND	ND	5.49	1.77
137	0.18	ND	ND	1.99	0.81
138	8.7	39.41	19.97	52.40	12.87
178	1.0	5.10	2.44	4.86	1.58
175	1.8	8.43	4.46	11.36	3.56
187/159	0.4	2.13	1.19	2.22	0.78
128	1.40	7.91	4.17	7.60	2.07
185	0.48	2.56	1.36	7.60	2.07
174	0.41	2.35	1.35	2.88	0.78
177	0.93	6.33	2.94	3.56	1.02
172	0.10	1.00	0.76	3.89	1.12
180	1.1	5.91	3.24	ND	ND
170	1.3	7.23	3.97	7.71	1.62
∑ PCBs	1101.4	920.08	568.15	7.34	2.01

^a The number used to designate each congener by International Union of Pure and Applied Chemistry (IUPAC).

^b Sample location see Table 1.

^c ND: not detectable.

Fig. 1. Relative composition of PCB homologues in a contaminated paddy field of WenTai area, China. A sample location see Table 1.

The $\sum$ PCBs burden of each sample was enriched in the tri- to penta-chlorinated congeners (Fig. 1). These three homolog groups consistently accounted for >79% of $\sum$ PCBs in the soil samples. When compared with $\sum$ PCBs in soil samples of S1, S3 and S5, the PCB residue in soil from Site A decreased 16% over 4 years (1993–1997), but changed little in the last 2 years (1997–1999).

In general, the disappearance of PCBs from the surface soil layer can be described by a simple first-order model:

$$C_{i,t} = C_{i,0} \exp(-K_i t) \quad (1)$$

where $C_{i,0}$ is the initial concentration of PCB congener in the soil, $C_{i,t}$ is the concentration of PCB congener in the soil ($\mu\text{g/kg}$) at time t , and K_i is first-order rate constant for disappearance of PCB congener from the soil layer. $C_{i,t}$ and t are the dependent and independent variables, respectively. K_i 's are parameters estimated from experimental data and dependent on the individual congener. Gan and Berthouex (1994) estimated the disappearance rate for PCB congeners in sludge amended farmland. Di-, tri- and tetra-chlorinated PCBs were found to have half-lives in the range of 4–58 months, while the more highly chlorinated PCBs were more persistent in the soil. Some congener (e.g. congener 180 and 177), the K approximately equals 0.000. In this study the data were insufficient to fit the model, but it can be seen that the concentrations of most di- to tetra-chlorinated PCB congeners showed a significant decrease compared with those of higher chlorinated PCB congeners (Fig. 1). Recent research has showed that there is a phenomenon of irreversible adsorption

for hydrophobic organic compounds (HOCs) in soil (Chen et al., 2000; Kan et al., 1997). This means that the desorption was time-varying kinetics, and the release of contaminants from the soils decreased or even stopped after a period (Connaughton et al., 1993). The concentrations of congener 180 and 177 in the soil samples indicated no decrease with time, and even showed some increase. It seemed that during the 6-year period, the paddy field near the pollution point probably had received additional contamination. Therefore, the pattern of highly chlorinated congeners distribution trended to increase.

It is interesting to speculate on the ultimate fate of the PCBs lost from the field. Based on known physico-chemical properties of PCBs, the most likely loss processes are volatilization, leaching and biodegradation. Alcock et al. (1993) showed that volatilization and subsequent long-range transport probably accounted for the bulk of this loss in soil. PCBs normally exhibit relatively low vapor pressures. Solely on the basis of vapor pressure, PCBs would be considered semi-volatile. However, PCBs are relatively insoluble and hydrophobic ($\log K_{OW} = 4-9$) and therefore can exhibit significant volatility from aqueous systems. Dunnivant and Elzermqn (1992) determined the Henry Law's Constants (HLCs) for several PCB congeners and calculated all HLCs of 209 congeners, and found that $-\log HLC$ ranged from 3.215 (PCB50) to 4.186 (PCB169). This shows that the highly chlorinated PCBs have lower HLC than low chlorinated PCBs and that the low chlorinated PCBs are more subject to evaporation from aqueous solutions than highly chlorinated PCBs. Some research has reported that significant amount of mono-, di- and tri-chlorinated biphenyls may be volatilized from Aroclar 1248 contaminated sediments at ambient environmental condition (Bushart et al., 1998). It was discovered that PCBs in sediments and particulate were highly susceptible to volatilization upon sediment drying. In the study, the paddy field are usually filled with water in the cultivation process and dried after harvest, therefore, volatilization was inevitable in these field.

It can be seen that even after 6 years the concentrations of PCBs in soil were far from reaching uniform (Table 1). The concentration of PCBs at Site B was about half those at Site A, although the pattern for these samples were similar. Since these two fields were

only separated by a narrow track of one-foot width, it is suggested that the transfer of PCBs in soil mainly resulted from the translocation of contaminated soil adsorbed PCBs, as the movement by volatilization and mobility through the pore water are rare.

Leaching is another reason to explain the congener transport in the environment. This study determined the leaching of PCBs in the paddy field. Because the environmental contamination by PCBs is in the form of complex mixture of many congeners and have not a uniform diffusivity, The pattern of PCB congener distribution will change with the sampling depth. Fig. 2 showed the vertical profiles of PCB congeners distribution at the two sites. The PCB concentrations in the soil showed maximal values at the surface and decreasing values sharply with sampling depth. Only trace amounts (<5 ng/g) of PCBs were observed in the 30–50 cm soil depth. The PCBs compositions also varied with depth. The low chlorinated PCB congeners were detected in all the samples with different depths, while the concentrations of highly chlorinated PCB congeners in deep layers were below the method detection limit. The equilibrium distribution coefficients (K_{OC}) of PCB congeners, which have different substituted chlorine number or position on the two benzene rings, are different from 1.25E5 to 6.3E6 l/kg (Jepsen and Lick, 1999). This may result in their different mobility in the soil. In general, a greater K_{OC} implies a weaker mobility. A laboratory study also showed that pore water was dominated by low chlorinated PCB congeners and sediment dominated by highly chlorinated congeners (Formica et al., 1988). Therefore, low chlorinated PCBs could migrate deeper soil layers through the pore water.

Furthermore, the alteration of the PCB congeners distribution observed in soil can also be attributed to biodegradation in the environment. The biodegradation and position of chlorine substituted. Biodegradation causes the disappearance of the lower chlorinated PCBs, and the degradation decreases with increasing chlorination (Furukawa et al., 1978).

3.2. PCBs pollution in air samples

Data are presented for three sets of PCB mixtures in vapor and particulate collected simultaneously (Table 3). The gaseous-phase and particle-phase were characterized by congeners with low chlorinated

Fig. 2. PCBs distribution in the different depth soils: (A) no. 1; (B) no. 2.

Table 3

The concentrations of PCB congeners in the gaseous-phase and particle-phase (ng/m³)

IUPAC no.	Gaseous-phase			Particle-phase		
	A1 ^a	A2	A3	P1	P2	P3
4	25.3	26.0	51.2	2.53	0.13	2.25
7	103.6	43.0	115.7	1.00	0.05	0.96
8	ND ^b	ND	ND	1.66	0.07	1.74
18/17	ND	ND	ND	0.78	0.34	1.23
16/32	ND	ND	ND	0.92	0.15	1.20
31/28	107.8	51.6	114.4	0.20	0.04	0.40
33	18.8	5.70	131.6	0.02	0.04	0.03
22	5.33	2.92	4.84	ND	ND	ND
52	66.6	27.2	71.6	0.03	0.06	0.09
49	21.9	9.46	24.8	0.03	0.07	0.09
47/48	14.5	7.18	10.3	0.01	0.02	0.02
37/42	22.7	18.2	64.7	ND	ND	ND
74	17.2	ND	20.0	ND	ND	ND
70	15.5	ND	3.60	ND	ND	ND
66	15.2	ND	24.2	ND	ND	ND
56/60	5.94	ND	4.11	ND	ND	ND
∑ PCBs	440.37	191.26	641.05	7.18	0.97	8.01

^a Sample location see Table 1.

^b ND: not detectable.

PCBs. The sum of PCB concentrations in the gaseous phase, which ranged from 191 to 640 ng/m³, was similar to those recorded in the gaseous fluxes for Lake Michigan (Zhang et al., 1999), however the congeners patterns were different from other European measurements in which penta- and hexa-chlorinated biphenyls were observed (Haugen et al., 1999). Particle-phase concentrations of PCBs in this study were very low and ∑ PCB ranged between 5 and 35 ng/m³.

The maximum ∑ PCB values in the gas-phase and particle-phase (samples A3 and P3, Table 1) were obtained from the residential area nearby the paddy field. There was an important difference in PCB concentrations pattern. The concentrations of individual PCB congeners varied considerably between the gas-phase and particulates. Generally, the values were considerably higher in the gas-phase than in the particle phase. From Table 3, it can be seen that the amount of PCBs on particulates was estimated as low as 1 to <2% of total air burden. The lower contribution of particulates to the total concentration of PCBs in the air samples has also been reported in other studies (Duinker and Bouchertall, 1989).

3.3. The rice uptake of PCBs

The various rice tissues were analyzed for PCBs (see Table 4). The PCBs samples of rice stalk and leaves were collected in 1993 and 1999, and those of grain and husk collected in 1993, 1997 and 1999. The PCB concentrations in the rice tissues ranged from ca. 1.8 to 130 ng/g DW, which was lower than those in the vegetables from the area of a capacitor plant in Serpukhov, Russia (Bobovnikova et al., 1993). The distributions of PCBs in rice tissues were similar in the samples of 1993 and 1999. PCBs concentrations in the rice tissues increased in the order: grain < stalk < husk < leaves. The maximum PCB concentrations (as much as 30–50 times in grain) were observed in the leaves. Leaves are exposed to atmosphere and can concentrate the contaminants from dry gaseous deposition, dry particle bound deposition and wet deposition. There was insignificant PCBs in the rice grain. The concentrations in grain were somewhat less than those found in wheat (*Triticum aestivum* L.), rye (*Secale cerea* L.) and barley (*Hordeum vulgare* L.) harvested in a 1972–1974 investigation in Germany, while PCBs were found in some samples at 10–130 ng/g DW (Arrifai and Acker, 1975).

Webber et al. (1994) found that there were differences among crops from PCB accumulation. Other workers also observed that the concentrations of PCB congeners differed greatly in various parts of vegetables (Chewe et al., 1997). Offenbaecher (1992) found an obvious PCB transfer from soil to carrots (*Daucus carotavar sativa* DC) especially with a higher enrichment of PCB no. 28 than no. 52. Much of the uptake was adsorption on the surfaces of root and small amounts of PCBs were found in the peeled fruit and the carrot foliage (O'Connor et al., 1990). In fact, PCBs in soil are very immobile and most of the PCBs in root may be adsorbed on the surface and not actually accumulated by the plant, therefore there is little translocation (O'Connor et al., 1990). However, volatilization of PCB from soil, landfills, road oil and other sources can result in measurable atmospheric pollution. It was reported that atmospheric deposition was thought to be responsible for 58–90% of Lake Superior and Michigan's PCB burden (Eisenreich et al., 1981; Jeremiason et al., 1994). Various lines of evidence indicated that polynuclear aromatic hydrocarbons (PAHs) concentrations in vegetation can

Table 4
Concentration of PCBs congeners in rice samples (ng/g¹)^a

IUPAC	G1	T1	H1	L1	G2	H2	G3	T3	H3	L3
4	ND ^b	ND	ND	ND	ND	ND	ND	0.26	0.22	0.33
7	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
8	ND	0.51	0.90	1.0	ND	ND	0.22	0.76	0.93	0.53
19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18/17	0.13	0.25	5.80	0.55	ND	ND	0.06	0.27	0.18	0.37
16/32	0.03	0.87	2.90	1.20	0.29	1.83	ND	0.07	ND	0.14
26/25	0.37	0.55	1.49	1.80	0.13	ND	0.04	0.18	0.20	0.20
31/28	0.39	3.00	7.20	1.90	1.28	3.49	0.08	0.05	0.52	2.77
33	ND	0.60	1.60	2.10	0.54	2.27	ND	0.38	0.41	0.52
22	ND	0.31	0.76	0.77	0.09	0.13	ND	ND	ND	ND
45	ND	ND	0.42	0.08	ND	ND	ND	0.04	ND	ND
52	0.26	1.70	2.20	11.60	4.33	12.42	ND	ND	0.26	0.77
49	0.05	0.84	1.00	6.60	0.77	ND	ND	0.56	0.19	0.57
47/48	0.23	0.75	1.40	4.50	ND	ND	ND	ND	0.20	0.40
44	0.04	1.10	1.60	9.60	0.24	2.61	ND	0.42	0.22	0.51
37/42	0.08	0.68	0.79	3.40	ND	ND	ND	ND	0.06	0.33
41/64	0.04	0.81	1.60	6.80	0.64	1.20	0.04	0.17	0.21	0.84
40	ND	ND	0.29	ND	ND	0.27	ND	ND	0.03	0.09
74	0.11	0.82	1.00	8.30	1.49	ND	0.02	0.11	0.12	0.73
70	0.12	0.94	1.60	12.10	1.71	ND	0.02	0.06	0.09	0.82
66	0.19	1.60	2.40	19.70	3.73	3.30	0.03	0.09	0.14	1.72
60/56	0.10	0.36	1.20	0.64	1.08	0.56	0.01	0.05	0.07	0.84
101	0.01	0.31	1.70	5.00	1.61	1.25	ND	0.28	0.41	2.35
99	ND	0.33	0.52	3.30	1.04	1.26	ND	ND	0.24	1.70
83	ND	ND	ND	0.25	ND	ND	ND	ND	ND	ND
97	ND	0.13	ND	2.10	1.19	0.88	ND	0.09	ND	1.35
87	ND	0.11	0.15	1.80	2.64	2.41	0.23	0.85	0.78	5.37
85	ND	0.25	ND	1.60	ND	ND	ND	ND	ND	ND
110	0.08	0.31	1.20	5.30	3.95	1.22	0.20	0.71	0.76	2.74
82	ND	0.07	0.24	0.69	1.14	ND	0.42	0.84	0.63	1.51
118/108	0.04	0.32	0.98	5.90	4.37	1.03	0.15	0.34	0.26	2.19
146	ND	0.07	0.47	2.00	1.46	ND	ND	ND	ND	0.59
153	0.04	0.08	0.34	1.30	1.32	0.30	0.04	0.10	0.10	0.54
141	ND	ND	0.06	0.38	ND	ND	ND	ND	ND	0.10
137	ND	ND	0.03	0.14	ND	ND	ND	ND	ND	ND
138	ND	0.12	0.89	3.60	2.94	0.54	ND	0.10	ND	0.90
178	ND	ND	0.20	0.34	ND	ND	ND	ND	ND	ND
175	ND	ND	ND	0.46	ND	ND	ND	ND	ND	ND
187/159	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
128	ND	ND	0.19	0.66	0.51	ND	ND	ND	ND	0.16
185	ND	ND	ND	0.14	ND	ND	ND	ND	ND	ND
174	ND	ND	ND	0.14	ND	ND	ND	ND	ND	ND
177	ND	ND	0.10	0.37	ND	ND	ND	ND	ND	ND
180	ND	ND	0.07	0.35	ND	ND	ND	ND	ND	0.08
170	ND	ND	0.09	0.41	ND	ND	ND	ND	ND	ND
Σ PCBs	2.34	17.700	43.57	129.00	38.50	36.98	1.55	6.78	7.24	32.08

^a Sample location see Table 1.

^b ND: not detectable.

Fig. 3. Scores of the first two principal components of normalized PCBs data in a contaminated paddy field of WenTai area samples.

be used as an indication of atmospheric deposition directly on the above-ground plant portions, and that uptake and translocation of soil-bound PAHs were negligible. With roughly similar properties between PAHs and PCBs, it is presumed that PCBs would show a similar result.

The results indicated that the total concentration of PCBs in soil from Site B was about half that in soil from Site A, the of PCBs contamination in leaves collected in the two fields were not significantly different. This also suggested that PCB concentrations in the rice are not greatly dependent on PCB concentrations in the soil. However, PCB concentrations in the rice leaves cannot be overlooked if livestock feed on them, as then PCBs can be bioconcentrated in human bodies through the food chain. From this point, the contaminated soils still represent a potential hazard to human health.

3.4. Principal components analysis (PCA)

For further data evaluation, environmental workers are interested in applying multivariate statistical methods to evaluate patterns of organic compounds in the environment (Swerev and Ballschmiter, 1989). These methods can reduce a complex dataset to a few principle components that represent the main composition of the sample. In this study, a multivariate

statistical technique—principal component analysis (PCA) with the SAS software was utilized to characterize PCBs profiles in the environmental samples. Sample data were normalized with the sum of PCB concentrations. The PCB concentrations below the detection limit were set to 0.

In these kind of plots, similarity of the compositions results in neighboring positions. Fig. 3 and Table 5 illustrate the PCB pattern in the WenTai samples on the principal components. Principal component 1, accounting for 35.4% of the variability, represents the degree of chlorination. It is loaded negatively by most di- to tetra-chlorobiphenyls and pos-

Table 5
Accumulated variance (%) explained by principal components in samples

Principal components	Proportion	Cumulative
PRIN1	0.35	0.35
PRIN2	0.18	0.54
PRIN3	0.09	0.63
PRIN4	0.07	0.70
PRIN5	0.05	0.76
PRIN6	0.05	0.80
PRIN7	0.04	0.85
PRIN8	0.03	0.88
PRIN9	0.03	0.91
PRIN10	0.02	0.93

itively by most penta- to heptachlorinated-biphenyls. Fig. 3 shows that PCB profile for the samples was clearly distinguished on the first principal component (PC): air and rice samples are all located on the negative side of the first PC, while most of the soil samples are found on the positive side. This indicated that air and rice are characterized by lower chlorinated PCBs and that the soil samples were characterized by higher chlorinated PCBs. The soil samples obtained at the various depths were characterized by different compositions of the mixtures of individual congeners. In Fig. 3, the soil sample point of 1993 was close to that of Aroclor 1242, which means that the contamination in the soil sample had similar congeners distribution with the pollution source, while those of 1997 and 1999 are somewhat toward Aroclor 1254 position, which had more higher chlorinated biphenyl congeners. All these observations indicated that the pattern of PCBs in soils after a few years cannot be considered to reflect the original pollution source. Meanwhile, the soil and rice samples scatter in Fig. 3, indicates that the distribution of PCBs in rice tissues has not direct relationship with soil pollution.

4. Conclusions

In conclusion, PCBs pollution in these paddy fields was quite serious. Even after 6 years the equilibrium of PCBs contamination between the paddy field and the pollution source or and the nearby paddy field was not reached. Although some of the lower chlorinated biphenyls disappeared in the past 6 years, the higher chlorinated biphenyls persisted in the field. The pattern of PCBs in soils could not be considered to reflect the original pollution source. Rice grown in the field was subject to some contamination by PCBs, but it does not appear significantly bioconcentrate PCBs from environmental system like several other plants. PCB concentrations in rice samples were not directly proportional to PCB concentrations in soil.

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