



Chlorobenzenes and organochlorinated pesticides in vegetable soils from an industrial site, China

Yang Song^{**}, Fang Wang^{**}, Yongrong Bian, Yinping Zhang, Xin Jiang^{*}

State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China.

E-mail: ysong@issas.ac.cn (Yang Song); wangfang@issas.ac.cn (Fang Wang)

Received 16 May 2011; revised 26 May 2011; accepted 02 June 2011

Abstract

Organochlorinated compounds are ubiquitous contaminants in the environment, especially in industrial sites. The objective of the work was to investigate whether a vegetable field near an industrial site is safe for vegetable production. The residues of chlorobenzenes (CBs), hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in a vegetable field which was near a chemical plant in China were characterized. Point estimate quotient was used for ecological risk assessment of the investigated site. The results showed that all CBs except monochlorobenzene (MCB) were detected in soils. The total concentrations of Σ CBs ranged from 71.06 to 716.57 ng/g, with a mean concentration of 434.93 ng/g. The main components of CBs in soil samples were dichlorobenzenes (DCBs), trichlorobenzenes (TCBs) and tetrachlorobenzenes (TeCBs), while for single congeners, 1,2,4-TCB had the highest concentration, which ranged from 13.21 to 210.35 ng/g with a mean concentration of 111.89 ng/g. Residues of hexachlorobenzene (HCB) in soil samples ranged from 0.9 to 11.79 ng/g, significantly lower than Σ DCB, Σ TCB and Σ TeCB. Concentrations of Σ HCHs and Σ DDTs in soils ranged from 11.32 to 55.24 ng/g and from 195.63 to 465.58 ng/g, respectively, of which the main components were α -HCH and *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE). Ecological risk assessment for the investigated site showed that the most potential risks were from TCBs and TeCBs, based on the hazard quotients. The higher residues of CBs and DDTs compared to the target values and the higher than 1 hazard quotients indicated that this area is not safe for vegetable production and thus soil remediation is needed.

Key words: chlorobenzenes; hexachlorocyclohexanes; dichlorodiphenyltrichloroethanes; degradation; risk assessment

DOI: 10.1016/S1001-0742(11)60720-1

Introduction

The pollution of chlorobenzenes (CBs) and organochlorinated pesticides (OCPs) is of worldwide concern due to their persistence, toxicity, bioaccumulation potential and long-range transportation (Zhu et al., 2005). The “dirty dozen”, including hexachlorobenzene (HCB) and dichlorodiphenyltrichloroethane (DDT), are listed as persistent organic pollutants (POPs) by the United Nations Environment Program (UNEP) (Wei et al., 2007a). Moreover, pentachlorobenzene (PeCB), α -hexachlorocyclohexane (α -HCH), β -hexachlorocyclohexane (β -HCH), and Lindane were listed as new POPs (SCPOP, 2009).

China is an important producer of CBs in the world, and accounts for more than 50% of the worldwide production. In 2003, the production of 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) in China was 12,000, 30,000 and 1000 tons, respectively (Zhang and Lu, 2005). In 2005, the production of DCBs and TCBs reached 66,000 ton and

5000 ton, respectively. HCB has never been used as pesticide in China, but it was still produced as an intermediate of pentachlorophenol in Tianjin Dagou Chemical Company until 2003 with a production quantity of about 2000 tons/yr (Wei et al., 2007a). Meanwhile, China produced and used millions of tons of OCPs before they were banned in 1983 (Li et al., 2001). China is the biggest producer and user of technical HCH in the world. The total production of HCH was estimated as 4.46 million metric tons before 1983 (Li et al., 1998). The total production of commercial DDT was more than 4.3×10^5 tons from 1951 to 1983 (Wei et al., 2007a). Even after the ban of technical HCH and DDT in 1983, Lindane (3200 tons totally) continued to be used in forest management until the year 2000 (Li et al., 2001). DDT was produced for export and for production of dicofol with a production quantity of 4000–6000 tons/yr (Wei et al., 2007a).

Due to the wide use of CBs, they have been detected in water, sediment, soil and sewage sludge (Cai et al., 2007; Wang et al., 1995; Wei et al., 2007b; Zhang et al., 2005; Zhou et al., 2009). However, reports on CBs residues in soils – especially the soils in industrial sites in China – are lacking. Although DDTs and HCHs have been detected in soil and in urban sites (Barriada-Pereira et al., 2005;

^{*} Corresponding author. E-mail: jiangxin@issas.ac.cn

^{**} These two authors contributed equally to this work.

Gong et al., 2004; Miglioranza et al., 2003), investigation of vegetable fields near OCPs-producing sites in China are hardly reported despite the existence of many vegetable fields close to factories in the suburban areas of China. It is doubtful whether these fields are safe for production of vegetables. Jan et al. (2009) reported that soils up to half a kilometer radius from an abandoned DDT factory were contaminated.

Ecological risk assessment has been considered as the best available tool for taking decisions on current situations and for predicting future risks in environmental protection (Maltby, 2006). The most rudimentary approach for evaluating the potential of chemicals to cause adverse effects is to compare the estimate of exposure with some threshold value (Solomon et al., 2000). The simplest comparison is a single-point estimate, such as the hazard quotient (HQ), which is defined as the quotient of the predicted environmental concentration (PEC) and the predicted no effect concentration (PNEC) (Domene et al., 2008; Zolezzi et al., 2005). To obtain PNEC, an assessment factor method is both suggested by US Environmental Protection Agency and European Commission Technical Guidance Document on Risk Assessment, mainly because of its advantage of easy-to-use (European Commission, 2003).

In the present study one chemical plant, which was a CBs and OCPs manufacturer, was selected to investigate the residues of organochlorinated compounds in the soil of a vegetable field near the plant. Point estimate quotient was used to evaluate their ecological risks. The objective was to investigate whether the fields near industrial sites were safe for vegetable production and the results will provide information for soil remediation and management of POPs in fields near industrial sites in China.

1 Materials and methods

1.1 Chemicals and reagents

Standards of monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), tetrachlorobenzene (TeCB), PeCB, HCB, DDT, dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD) and HCHs, purity > 99.5%, were obtained from Dr. Ehrenstorfer (Augsburg, Germany). All other solvents, purchased from Nanjing Chemical Factory (China), were of analytical grade. Sodium sulphate (Na_2SO_4) was oven-dried at 150°C for 2 hr to act as desiccant. Silica gel was activated in an oven at 225°C for 12 hr, deactivated by adding 5% deionized water, and then mixed with equivalent amounts of sulfuric acid to prepare sulphonated silica gel.

1.2 Sampling

The selected chemical plant is one of the biggest manufacture of CBs and pesticide in China. It produces DDT to date for use in the production of dicofol. The main CBs products were 1,2-/1,3-/1,4-DCB and 1,2,3-/1,2,4-TCB. It also produces nitrobenzene, aniline, pyrethrum and other intermediates or preparations. With urbanization, all the areas surrounding the chemical plant have been converted

to either residential zones or industrial zones with small factories except for one vegetable field which extends for 1 km to the south of the factory (Fig. 1). The samples were collected from this vegetable field. Soil samples were collected from surface layers (0–10 cm), then sieved (≤ 2 mm) and stored at 4°C before analysis. The detailed sample information is listed in Table 1.

1.3 CBs and OCPs analysis

Soil samples were extracted by accelerated solvent extraction (Dionex ASE 200, USA). Soil sample of 10 g was homogenized with 5 g diatomaceous earth. The extraction was performed at 90°C and 10 MPa with hexane/acetone (4:1, V/V) as the extraction solvent. The extract was concentrated to about 2 mL by a rotary vacuum evaporator at 45°C and then applied to a sulphonated silica gel/anhydrous sodium sulfate column followed by elution with 15 mL hexane/dichloromethane (9:1, V/V). Finally, the eluate was concentrated to 1 mL for subsequent GC analysis. All samples were prepared and analyzed in triplicates.

The determination of analytes was carried out with a gas chromatography system (Agilent 6890 GC, USA) equipped with a ^{63}Ni microcell electron capture detector (μECD) and a tower 100 position 7683 autosampler in the splitless mode. The separation occurred on a 30 m \times 0.32 mm i.d. DB-5 capillary column with a film thickness of 0.25 μm and at a pressure of 48.4 kPa. Nitrogen was used as carrier gas at a flow rate of 1.5 mL/min. The column temperature was programmed from 50°C (1 min) to 180°C (1 min) at 10°C/min and then to 250°C (1 min) at 8°C/min and finally to 280°C (1 min) at 3°C/min. The injector and detector temperature were 220 and 300°C, respectively. A sample of 1 μL was injected with a syringe and concentrations of individual organochlorinated

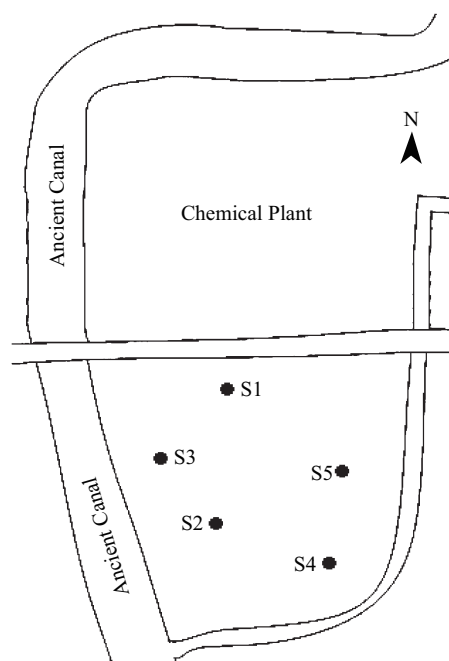


Fig. 1 Sampling sites (S1–S5) in the vegetable field near the chemical plant.

Table 1 Soil sample information and soil basic physico-chemical properties

Sample No.	Sample information	pH (H ₂ O)	OM (g/kg)	TOC (%)	Mechanical component (%)		
					2–0.05 mm	0.05–0.002 mm	< 0.002 mm
S1	Vegetable soil	7.81	17.17	1.00	49.39	43.80	6.81
S2	Vegetable soil	8.00	21.31	1.24	38.52	52.12	9.36
S3	Pond sediment	7.43	20.58	1.19	46.28	45.78	7.94
S4	Vegetable soil	6.85	16.34	0.95	38.85	47.27	13.88
S5	Vegetable soil	7.37	26.39	1.53	39.29	46.83	13.88

OM: organic matter; TOC: total organic carbon.

Table 2 Toxicity data of compounds and the calculated PNEC in soil

Compound	Species	EC ₅₀ (μg/g)	NOEC (μg/g)	PNEC _{soil} (μg/g)	
				EC ₅₀	NOEC
1,2-DCB	Rattus norvegicus Norway Rat	151.60	10.00	0.152	0.100
1,4-DCB	Lactuca sativa Lettuce	213.00	10.00	0.213	0.100
1,2,3-TCB	Lactuca sativa Lettuce	1.00	1.00	0.001	0.010
1,2,4-TCB	Lactuca sativa Lettuce	48.00	10.00	0.048	0.100
1,3,5-TCB	Lactuca sativa Lettuce	115.00	1.00	0.115	0.010
1,2,3,4-TeCB	Lactuca sativa Lettuce	32.00	3.20	0.032	0.032
1,2,4,5-TeCB	Lactuca sativa Lettuce	1.30	1.00	0.001	0.010
PeCB	Lactuca sativa Lettuce	56.00	3.20	0.056	0.032
HCB	Lactuca sativa Lettuce	1000.00	10.00	1.000	0.100
HCH	Vicia faba Broadbean	1000.00	2.20	1.000	0.022
DDT	Trifolium repens Dutch Clover	1000.00	1.00	1.000	0.010

DCB: dichlorobenzene; TCB: trichlorobenzene; TeCB: tetrachlorobenzene; PeCB: pentachlorobenzene; HCB: hexachlorobenzene; HCH: hexachloro-cyclohexane; DDT: dichlorodiphenyltrichloroethane; EC₅₀: half maximal effective concentration; NOEC: no observed effect concentration; PNEC_{soil}: predicted no effect concentration in soil.

compounds were quantified according to the peak areas of the respective external standards following calibration with authentic standards.

1.4 Ecological risk assessment

Hazard quotient (HQ) was used to evaluate the ecological risk in the vegetable field (Eq. (1)):

$$HQ = \frac{PEC_{soil}}{PNEC_{soil}} = \frac{PEC_{soil}}{C_{toxicity}/AF} \quad (1)$$

where, PEC_{soil} (μg/g) was the predicted environmental concentration of the compound in soil, which equals to the measured concentration; $PNEC_{soil}$ (μg/g) was the predicted no effect concentration in soil; $C_{toxicity}$ (μg/g) was the toxicity data of the compound for a certain species and AF was assessment factor. To reduce the uncertainty, $PNEC_{soil}$ was calculated by the lowest half maximal effective concentration (EC₅₀) and no observed effect concentration (NOEC), respectively. As shown in Table 2, all the toxicity data of EC₅₀ and NOEC were obtained from the ECOTOXicology database (ECOTOX) of US EPA (2001). The assessment factor method, which select the lowest reported value and divides it by an assessment factor, was used to extrapolate laboratory toxicity data to reflect the field situation. According to European Chemicals Bureau (2003) and European Commission (2003), the assessment factor of 1000 was used when calculating $PNEC_{soil}$ by EC₅₀ and an assessment factor of 100 was used when calculating $PNEC_{soil}$ by NOEC since there was only one trophic level long-term data.

1.5 Quality control and data analysis

To estimate the recovery of CBs and OCPs residues in soil, a recovery study was carried out by spiking 2 μg of each compound to 10 g soil. The recoveries for 3 replicates of CBs from soil increased from 60.76% to 91.56% with increasing number of chlorine atoms of the CBs. The recoveries of HCHs ranged from 85.61% to 95.11% and of DDTs ranged from 89.59% to 98.82%.

All concentrations were expressed on an oven-dried (105°C) weight basis and means were expressed in arithmetic value. All the data were analyzed by SPSS 17.0 software package for the purpose of statistics and the significance level was $p < 0.05$.

2 Results and discussion

2.1 CBs in soils

The concentrations of CBs in the investigated field are shown in Table 3. Except for MCB, nearly all the CBs congeners were detected in the soil samples. The fact that MCB was not detected in all soil samples might be due to its high vapor pressure which leads to high volatilization (Brahushi et al., 2002). The total concentrations of Σ CBs ranged from 71.06 to 716.57 ng/g with a mean concentration of 434.93 ng/g. As shown in Table 4, the mean concentration of Σ CBs in this study was significantly higher than other investigated soil samples (Ding et al., 1992; Wang et al., 1995; Zhang et al., 2005; Zhou et al., 2007). According to the guide for soil remediation of the Netherlands, the Σ CBs were significantly higher than the target value (Table 3).

Compared to lower chlorinated benzenes, the concen-

Table 3 CBs concentrations in soils of a vegetable field near a chemical plant and the comparison with different guidelines

Compound	CBs concentrations in soil (ng/g)					Mean	Target value
	S1	S2	S3	S4	S5		
1,2-DCB	21.05	28.83	187.48	9.14	23.03	53.91	50.00 ^a
1,3-DCB	32.29	22.85	144.64	6.25	51.16	51.44	50.00 ^a
1,4-DCB	51.04	38.68	127.96	13.99	115.75	69.48	50.00 ^a
1,2,3-TCB	43.66	76.68	131.8	6.41	42.71	60.25	50.00 ^a
1,2,4-TCB	80.66	145.85	210.35	13.21	109.37	111.89	50.00 ^a
1,3,5-TCB	1.30	1.89	1.93	0.40	0.53	1.21	50.00 ^a
1,2,3,4-TeCB	92.51	236.4	133.41	16.26	42.02	104.12	50.00 ^a
1,2,3(4),5-TeCB	23.24	60.41	33.07	3.42	9.51	25.93	50.00 ^a
PeCB	14.03	6.20	n.d.	0.88	1.08	5.55	50.00 ^a
HCB	8.35	5.04	11.79	1.10	0.90	5.44	50.00 ^a
DCBs	104.38	90.36	355.61	29.37	189.94	153.93	–
TCBs	125.62	224.41	344.08	20.02	152.61	173.35	–
TeCBs	115.75	296.8	166.49	19.68	51.53	130.05	–
ΣCBs	368.14	622.82	716.57	71.06	396.07	434.93	30.00 ^b

n.d.: below the detection limit (0.01 ng/g); –: no standard value.

DCBs = 1,2 + 1,3 + 1,4-DCB; TCBs = 1,2,3 + 1,2,4 + 1,3,5-TCB; TeCBs = 1,2,3,4 + 1,2,3(4),5-TeCB; ΣCBs = MCB + DCBs + TCBs + TeCBs + PeCB + HCB.

^a Canadian Soil Quality Guidelines for Agricultural Land Use (2007).

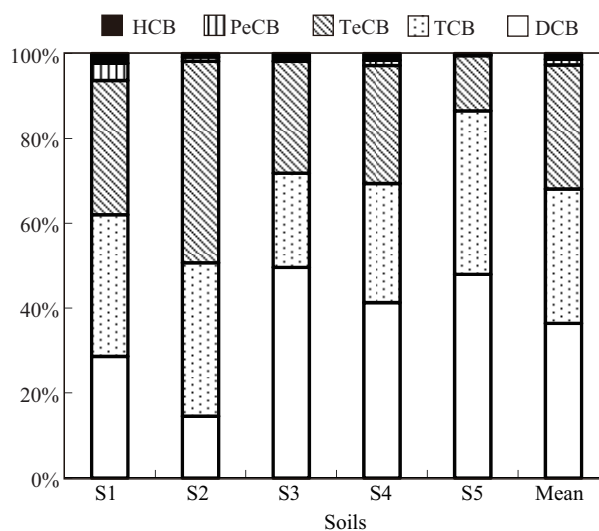
^b Circular on target values and intervention values for soil remediation of the Netherlands 2000 and 2009.

Table 4 Comparison of ΣCBs in the investigated site with other reports

Location	Samples	ΣCBs (ng/g)		Reference
		Mean	Range	
Vegetable field, China	Vegetable soil	434.93	71.06–716.57	This study
Beijing industry zone, China	Soil	18.16	0.23–51.15	Zhou et al., 2007
Hangzhou City, China	Vegetable soil	49.00	30.50–82.30	Zhang et al., 2005
Woburn, UK	Field soil	7.65	2.75–18.90	Wang et al., 1995
Niagara falls/Erie county, USA	Soil	8.45	2.84–12.29	Ding et al., 1992
Tonghui River, China	Sediment	562.60	18.20–1827.70	Zhou et al., 2009
Pearl River, China	Sediment	19.40	7.83–40.09	Wei et al., 2007b
Eleven cities in China	Sewage sludge	1100.00	10.00–6900.00	Cai et al., 2007

trations of the higher chlorinated benzenes such as HCB and PeCB were much lower (Table 3). The concentration of HCB in the investigated field was the same as that in Taihu Lake region (Wang et al., 2007) and Northeastern China (Gong et al., 2004). For single congeners, the concentration of CBs was in the order of 1,2,4-TCB > 1,2,3,4-TeCB > 1,4-DCB > 1,2,3-TCB. According to Canadian soil quality guidelines for agricultural land use, the main contaminants in this field were 1,2,4-TCB and 1,2,3,4-TeCB. However, as shown in Fig. 2, the main components of CBs in soil samples were DCBs, TCBs and TeCBs, accounting for 36.42%, 31.67% and 29.26% respectively. This is consistent with the results of Zhou et al. (2007), who determined DCBs are the major components in Beijing industrial zone.

The sample S3, which was collected from pond sediment (Table 1), showed significantly higher concentrations of DCBs and TCBs than other soil samples (Table 3), indicating that DCBs and TCBs were resistant to biodegradation under anaerobic conditions (Field and Sierra-Alvarez, 2008). Another reason might be that the higher chlorinated benzenes, especially HCB and PeCB, were readily reductively dechlorinated to lower chlorobenzenes under anaerobic conditions (Hirano et al., 2007). The fact that PeCB was not detected in S3 is consistent with the fact that dechlorination of PeCB occurs more easily than that of HCB (Beurskens et al., 1994).

**Fig. 2** Percentage composition of different CBs in soils.

2.2 HCHs and DDTs in soils

Since the investigated chemical plant still produces DDT for export and for production of dicofol, HCHs and DDTs in soils from the vegetable field were also detected. As shown in Table 5, except for δ -HCH in samples S3 and S5, all the HCHs and DDTs were detected in soil samples. Among all the pesticide concentrations, ΣDDTs (DDD, DDE and DDT) showed significantly higher concentra-

Table 5 HCHs and DDTs in the vegetable soils near a chemical plant and the comparison with different guidelines

Compound	HCHs or DDTs (ng/g)						China ^a		The Netherlands ^b	Canada ^c
	S1	S2	S3	S4	S5	Mean	First grade	Second grade	Target value	Agricultural land use
α -HCH	10.41	17.42	10.75	4.74	5.97	9.86	–	–	3.00	–
β -HCH	8.52	14.97	8.73	1.84	5.65	7.94	–	–	9.00	–
γ -HCH	5.89	10.46	8.81	3.55	4.07	6.56	–	–	0.05	–
δ -HCH	14.58	12.38	n.d.	1.20	n.d.	9.39	–	–	–	–
Σ HCHs	39.40	55.24	28.29	11.32	15.69	29.99	50.00	500.00	10.00	10.00
<i>o,p'</i> -DDE	39.26	71.96	55.05	6.61	21.58	38.89	–	–	–	–
<i>p,p'</i> -DDE	246.65	227.56	102.41	80.12	209.38	173.22	–	–	–	–
<i>p,p'</i> -DDD	48.19	29.58	70.72	19.58	34.14	40.44	–	–	–	–
<i>o,p'</i> -DDT	4.26	34.03	2.79	14.90	24.55	16.11	–	–	–	–
<i>p,p'</i> -DDT	38.08	102.45	28.00	74.43	134.68	75.53	–	–	–	–
Σ DDTs	376.44	465.58	258.98	195.63	424.33	344.19	50.00	500.00	10.00	700.00

n.d.: below the detection limit (0.01 ng/g); –: no standard value.

HCH: hexachlorocyclohexane; DDE: dichlorodiphenyldichloroethylene; DDD: dichlorodiphenyldichloroethane; DDT: dichlorodiphenyltrichloroethane; Σ HCHs = α + β + γ + δ -HCH; Σ DDTs = *o,p'*-DDE + *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT.

^a: Environmental quality standards for soils of China (GB15618-1995); ^b: circular on target values and intervention values for soil remediation of the Netherlands (2000, 2009); ^c: Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (2007).

tions than Σ HCHs ($p < 0.05$). The Σ DDTs concentrations are higher than those reported in Taihu Lake region (Wang et al., 2007) and Northeastern China (Gong et al., 2004) but lower than those in an abandoned DDT manufacturing factory in Pakistan (Jan et al., 2009). Both concentrations of the Σ HCHs and Σ DDTs were lower than those in an industrial site near Beijing (Yang et al., 2010). Generally, the Σ HCHs concentrations were lower than the first grade of the Environmental Quality Standards for Soils of China but higher than the target value of the Netherlands and agricultural land use guideline of Canada (Table 5). The DDTs contents in all the samples were higher than the first grade of Environmental Quality Standards of China and the target value of the Netherlands, showing that this site was moderately polluted.

2.3 Source and degradation of CBs, HCHs and DDTs

CBs are semi-volatile organic contaminants (Zhang et al., 2005) and most of them, especially the lower chlorinated benzenes, are used as solvents or intermediates in the synthesis of other chemicals but are not applied directly to vegetables as pesticides (Zhou et al., 2009). Therefore, the air-soil equilibrium should be a main source of CBs for the investigated field, which is located within 1 km from the chemical plant. The main products of CBs in the chemical plant near the investigated field was 1,2-/1,3-/1,4-DCB; 1,2,3-/1,2,4-TCB. This can explain the high residues of 1,2,4-TCB that were detected in the soils (Table 3). The concentrations of HCB, PeCB and 1,3,5-TCB were much lower since they were not produced (Table 3), indicating that the soil pollution was related to the production of the compounds (Jan et al., 2009). However, the concentration of 1,2,3,4-TeCB in the investigated field was as high as that of 1,2,4-TCB even though it was not produced in the chemical plant. Therefore, further investigation is needed to establish the source of the pollution. Another source of CBs might be the water used for irrigation. Canal water near the chemical plant was used to irrigate the vegetable field. However, wastewater from the plant was discharged into this canal after treatment. This could be inferred from

the fact that 487.56 $\mu\text{g/L}$ of Σ CBs was detected in the canal water.

Since HCHs were banned in 1983 (Li et al., 1998), the residues of HCHs in the investigated field should arise from historical use, given that HCHs were not detected in the canal water mentioned above. Generally, technical HCH contains isomers in the following percentages: α -HCH, 55%–80%; β -HCH, 5%–14%; γ -HCH, 8%–15%; δ -HCH, 2%–16% and ϵ -HCH, 3%–5%, while Lindane consists almost entirely pure γ -HCH (Willett et al., 1998). According to Willett et al. (1998) the detection of β -HCH was probably indicative of local technical HCH contamination because the β -HCH isomer is the most persistent with respect to microbial degradation and has the lowest volatility. Moreover, the ratios of α -HCH/ γ -HCH in the five samples ranged from 1.22 to 1.7, which were much lower than those of technical HCH, indicating that the source of HCHs in this field might not only be technical HCH but also Lindane (Qiu et al., 2004).

After the ban of DDT in China in 1983, dicofol related DDT was only used in cotton fields (Yang et al., 2008). Thereby, the residues of DDX in the vegetable field might arise from (1) historical use of DDT given its long time persistence in soil (Zhang et al., 2006), (2) the air-soil equilibrium since the site is near to a chemical plant which still produces DDT, and (3) water irrigation since Σ DDTs with a concentration of 32.24 $\mu\text{g/L}$ was detected in the canal water. However, as shown in Fig. 3, the ratio of (*p,p'*-DDE+*p,p'*-DDD)/*p,p'*-DDT of all the soil samples ranged from 1.34 to 7.74, indicating that the main fate of DDT in this area was degradation (Miglioranza et al., 2003).

Generally, DDT could be reductively dechlorinated to DDD and dehydrochlorinated to DDE (Wang et al., 2007). The ratio of *p,p'*-DDE/*p,p'*-DDT was significantly higher than that of *p,p'*-DDD/*p,p'*-DDT in Fig. 3 ($p < 0.05$), demonstrating that the main degradation pathway of DDT in this field was dehydrochlorination to DDE. However, sample S3 showed a higher ratio of *p,p'*-DDD/*p,p'*-DDT than other samples since it was collected from pond sediment. This is because anaerobic conditions exist in

Table 6 Hazard quotient (HQ) calculated by dividing measured concentrations by $PNEC_{soil}$

Compound	HQ											
	$PNEC_{soil} = EC_{50}/1000$						$PNEC_{soil} = NOEC/100$					
	S1	S2	S3	S4	S5	Mean	S1	S2	S3	S4	S5	Mean
1,2-DCB	0.139	0.190	1.237	0.060	0.152	0.356	0.211	0.288	1.875	0.091	0.230	0.539
1,3-DCB	0.213	0.151	0.954	0.041	0.337	0.339	0.323	0.229	1.446	0.063	0.512	0.514
1,4-DCB	0.240	0.182	0.601	0.066	0.543	0.326	0.510	0.387	1.280	0.140	1.158	0.695
1,2,3-TCB	43.660	76.680	131.800	6.410	42.710	60.252	4.366	7.668	13.180	0.641	4.271	6.025
1,2,4-TCB	1.680	3.039	4.382	0.275	2.279	2.331	0.807	1.459	2.104	0.132	1.094	1.119
1,3,5-TCB	0.011	0.016	0.017	0.003	0.005	0.011	0.130	0.189	0.193	0.040	0.053	0.121
1,2,3,4-TeCB	2.891	7.388	4.169	0.508	1.313	3.254	2.891	7.388	4.169	0.508	1.313	3.254
1,2,3(4),5-TeCB	17.877	46.469	25.438	2.631	7.315	19.946	2.324	6.041	3.307	0.342	0.951	2.593
PeCB	0.251	0.111	0.000	0.016	0.019	0.079	0.438	0.194	0.000	0.028	0.034	0.139
HCB	0.008	0.005	0.012	0.001	0.001	0.005	0.084	0.050	0.118	0.011	0.009	0.054
HCH	0.039	0.055	0.028	0.011	0.016	0.030	1.791	2.511	1.286	0.515	0.713	1.363
DDT	0.042	0.136	0.031	0.089	0.159	0.092	4.234	13.648	3.079	8.933	15.923	9.163

$PNEC_{soil}$ for 1,3-DCB was the data the same as 1,2-DCB; the $PNEC_{soil}$ for 1,2,3(4),5-TeCB was the data for 1,2,4,5-TeCB.

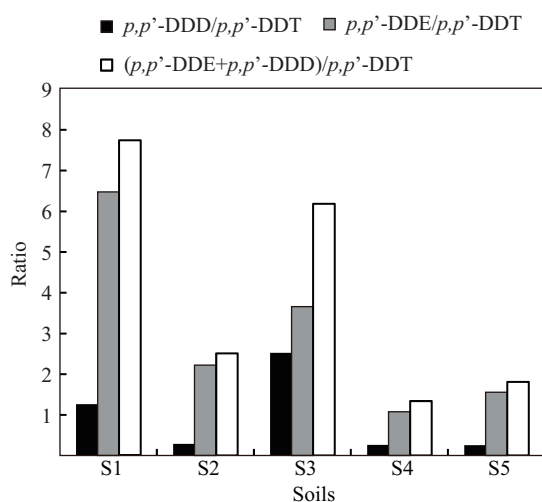


Fig. 3 Ratios of p,p' -DDD/ p,p' -DDT, p,p' -DDE/ p,p' -DDT and $(p,p'$ -DDE+ p,p' -DDD)/ p,p' -DDT in soils.

the pond bed and it is easier for reductive dechlorination of DDT to occur under anaerobic conditions than under aerobic conditions (Yao et al., 2006).

2.4 Risk characterization

Point estimate quotients are commonly used for ecological risk assessment of contaminated sites due to their simplicity, transparency and low data requirement (Jager et al., 2001; Zolezzi et al., 2005). PNEC is the concentration at which no harmful effects on the environment are expected. Generally, the HQ value < 1 means that there's no risk for the site and the HQ value > 1 could not accurately indicate real risk, therefore another more complex assessment must follow (Domene et al., 2008).

As shown in Table 6, when using the EC_{50} data, the compound with the highest HQ was 1,2,3-TCB, followed by 1,2,3(4),5-TeCB, 1,2,3,4-TeCB and 1,2,4-TCB. When using the NOEC data, however, the compound with the highest HQ was DDT, followed by 1,2,3-TCB, 1,2,3,4-TeCB, 1,2,3(4),5-TeCB, HCH and 1,2,4-TCB, all of which showed HQ > 1 . HCB showed the lowest potential risk based on the lowest HQ. Both methods indicated that 1,2,3-TCB, 1,2,4-TCB, 1,2,3,4-TeCB and 1,2,3(4),5-TeCB were the most potentially risky compounds and therefore need further assessment. Although the concentration of

CBs was in the order of 1,2,4-TCB/1,2,3,4-TeCB $>$ 1,2,3-TCB, the potential risk was in the order of 1,2,3-TCB $>$ 1,2,4-TCB/1,2,3,4-TeCB, indicating that risk assessment is necessary for decision making and soil remediation (Solomon et al., 2000). Nonetheless, the uncertainty was unavoidable in assessment. For instance, the HQ values for 1,2,3-TCB, 1,2,4-TCB and 1,2,3(4),5-TeCB calculated by EC_{50} were higher than those calculated by NOEC, while other compounds showed the converse results, especially for HCH and DDT. The potential risk is mostly related to the assessment factor (Zolezzi et al., 2005) and the toxicity data. Therefore, more toxicity data and more sensitive methods such as species sensitivity distribution method should be used for further risk assessment (Solomon et al., 2000).

3 Conclusions

Except for MCB, all the congeners of CBs were detected in the vegetable field soils near the chemical plant. HCHs and DDTs were also detected in vegetable soils. Based on the hazard quotient assessment, TCBs and TeCBs showed significantly higher potential ecological risk than other compounds. The contamination of the vegetable field was related to the production of the chemical plant. Therefore, strict management should be applied in site selection of a chemical plant and soil remediation measures should be undertaken on vegetable fields near industrial sites.

Acknowledgments

This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KZCX2-EW-QN403), the National Natural Science Foundation of China (No. 41030531, 40921061), and the Natural Science Foundation of Jiangsu Province (No. BK2010608).

References

- Barriada-Pereira M, González-Castro M J, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D, Fernández-Fernández E, 2005. Organochlorine pesticides accumulation and degradation products in vegetation samples of a contaminated area in Galicia (NW Spain). *Chemosphere*, 58(11): 1571–1578.
- Beurskens J E M, Dekker C G C, Van den Heuvel H, Swart M,

- De Wolf J, Dolfig J, 1994. Dechlorination of chlorinated benzenes by an anaerobic microbial consortium that selectively mediates the thermodynamic most favorable reactions. *Environmental Science & Technology*, 28(4): 701–706.
- Brahushi F, Dorfler U, Schroll R, Feicht E, Munch J C, 2002. Environmental behavior of monochlorobenzene in an arable soil. *Fresenius Environmental Bulletin*, 11(9): 599–604.
- Cai Q Y, Mo C H, Wu Q T, Zeng Q Y, Katsoyiannis A, 2007. Occurrence of organic contaminants in sewage sludges from eleven wastewater treatment plants, China. *Chemosphere*, 68(9): 1751–1762.
- Ding W H, Aldous K M, Briggs R G, Valente H, Hilker D R, Connor S et al., 1992. Application of multivariate statistical analysis to evaluate local sources of chlorobenzene congeners in soil samples. *Chemosphere*, 25(5): 675–690.
- Domene X, Ramírez W, Mattana S, Alcañiz J M, Andrés P, 2008. Ecological risk assessment of organic waste amendments using the species sensitivity distribution from a soil organisms test battery. *Environmental Pollution*, 155(2): 227–236.
- European Commission, 2003. Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances, Commission Regulation No. 1488/94 on Risk Assessment for Existing Substances and Directive 98/8/EC of the European Parliament and of the Council Concerning the Placing of Biocidal Products on the Market. Part II. Technical Guidance Document on Risk Assessment. Brussels, Belgium, UK. 328.
- European Chemicals Bureau, 2003. 1,2,4-Trichlorobenzene European Union Risk Assessment Report. European Commission Joint Research Centre. EUR 20540 EN. 73–74.
- Field J A, Sierra-Alvarez R, 2008. Microbial degradation of chlorinated benzenes. *Biodegradation*, 19(4): 463–480.
- Gong Z M, Tao S, Xu F L, Dawson R, Liu W X, Cui Y H et al., 2004. Level and distribution of DDT in surface soils from Tianjin, China. *Chemosphere*, 54(8): 1247–1253.
- Hirano T, Ishida T, Oh K, Sudo R, 2007. Biodegradation of chlordane and hexachlorobenzenes in river sediment. *Chemosphere*, 67(3): 428–434.
- Jager T, Vermeire T G, Rikken M G J, van der Poel P, 2001. Opportunities for a probabilistic risk assessment of chemicals in the European Union. *Chemosphere*, 43(2): 257–264.
- Jan M R, Shah J, Khawaja M A, Gul K, 2009. DDT residue in soil and water in and around abandoned DDT manufacturing factory. *Environmental Monitoring and Assessment*, 155(1–4): 31–38.
- Li Y F, Cai D J, Shan Z J, Zhu Z L, 2001. Gridded usage inventories of technical hexachlorocyclohexane and lindane for China with 1/6° latitude by 1/4° longitude resolution. *Archives of Environmental Contamination and Toxicology*, 41(3): 261–266.
- Li Y F, Cai D J, Singh A, 1998. Technical hexachlorocyclohexane use trends in China and their impact on the environment. *Archives of Environmental Contamination and Toxicology*, 35(4): 688–697.
- Maltby L, 2006. Environmental risk assessment. In: *Chemicals in the Environment: Assessing and Managing Risk* (Hester R E, Harrison R M, eds.). The Royal Society of Chemistry Publishing, Cambridge, UK. 84–101.
- Miglioranza K S B, De Moreno J E A, Moreno V J, 2003. Dynamics of organochlorine pesticides in soils from a south-eastern region of Argentina. *Environmental Toxicology and Chemistry*, 22(4): 712–717.
- Qiu X H, Zhu T, Li J, Pan H S, Li Q L, Miao G F et al., 2004. Organochlorine pesticides in the air around the Taihu Lake, China. *Environmental Science & Technology*, 38(5): 1368–1374.
- SCPOP, 2009. The fourth Meeting of Stockholm Convention on Persistent Organic Pollutants. <http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx>.
- Solomon K, Giesy J, Jones P, 2000. Probabilistic risk assessment of agrochemicals in the environment. *Crop Protection*, 19(8–10): 649–655.
- US EPA, 2001. ECOTOX: Ecological Toxicity Database, mid-continent ecology division. National Health and Environmental Effects Research Laboratory.
- Wang F, Jiang X, Bian Y R, Yao F X, Gao H J, Yu G F et al., 2007. Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China. *Journal of Environmental Sciences*, 19(5): 584–590.
- Wang M J, McGrath S P, Jones K C, 1995. Chlorobenzenes in field soil with a history of multiple sewage-sludge applications. *Environmental Science & Technology*, 29(2): 356–362.
- Wei D B, Kameya T, Urano K, 2007a. Environmental management of pesticidal POPs in China: Past, present and future. *Environment International*, 33(7): 894–902.
- Wei T L, Jia X S, Du Q P, Du Q P, Lai Z N, Pang S X et al., 2007b. Chlorobenzenes in the waters, sediments and aquatic animals from the Pearl River Estuary. *Acta Scientiae Circumstantiae*, 27(10): 1717–1726.
- Willett K L, Ulrich E M, Hites R A, 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environmental Science & Technology*, 32(15): 2197–2207.
- Yang L Y, Xia X H, Liu S D, Bu Q W, 2010. Distribution and sources of DDTs in urban soils with six types of land use in Beijing, China. *Journal of Hazardous Materials*, 174(1–3): 100–107.
- Yang X L, Wang S S, Bian Y R, Chen F, Yu G F, Gu C G et al., 2008. Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu Province, China. *Journal of Hazardous Materials*, 150(1): 92–98.
- Yao F X, Jiang X, Yu G F, Wang F, Bian Y R, 2006. Evaluation of accelerated dechlorination of *p,p'*-DDT in acidic paddy soil. *Chemosphere*, 64(4): 628–633.
- Zhang H B, Luo Y M, Zhao Q G, Wong M H, Zhang G L, 2006. Residues of organochlorine pesticides in Hong Kong soils. *Chemosphere*, 63(4): 633–641.
- Zhang J Y, Zhao W, Pan J, Qiu L M, Zhu Y M, 2005. Tissue-dependent distribution and accumulation of chlorobenzenes by vegetables in urban area. *Environment International*, 31(6): 855–860.
- Zhang M Y, Lu Y M, 2005. Market analysis and development trend of chlorobenzenes. *Chlor-Alkali Industry*, (1): 26–32.
- Zhou X, Deng S B, Huang J, Yu G, Lv H L, 2009. Occurrence and distribution of chlorobenzenes in the Tonghui River of Beijing, China. *Archives of Environmental Contamination and Toxicology*, 57(1): 32–41.
- Zhou X, Yu G, Huang J, Zhang Z L, Hu H Y, 2007. Residues and distribution characters of chlorobenzenes in soil and plants from Beijing southeast chemical industry zone. *Environmental Science*, 28(2): 249–254.
- Zhu Y F, Liu H, Xi Z Q, Cheng H X, Xu X B, 2005. Organochlorine pesticides (DDTs and HCHs) in soils from the outskirts of Beijing, China. *Chemosphere*, 60(6): 770–778.
- Zolezzi M, Cattaneo C, Tarazona J V, 2005. Probabilistic ecological risk assessment of 1,2,4-trichlorobenzene at a former industrial contaminated site. *Environmental Science & Technology*, 39(9): 2920–2926.