Levels and distribution of organochlorine pesticides and hexachlorobutadiene in soils and terrestrial organisms from a former pesticide-producing area in Southwest China

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Abstract The contamination of organochlorine pesticides (OCPs) and hexachlorobutadiene (HCBD) in soils, plants, and terrestrial fauna from a former pesticide-producing area in Southwest China was investigated. High levels of OCP residues (Σ HCHs and Σ DDTs of 3.89–13,386 and 23.3–11,186 ng g⁻¹ dw, respectively) were found in the soils within the producing factory, indicating that the former pesticide factory brownfield site poses a high environment risk and that effective soil remediation is needed. The OCP concentrations in soils surrounding the pesticide factory were 1–2 orders of magnitude higher than in the other agricultural areas from China. Grass, vegetables, and tree leaves from the surrounding areas of the point source showed moderate OCP pollution, which was likely to be causing potential negative impacts on terrestrial ecosystem. OCP levels in terrestrial species from the studied area including insects, free-range chickens and birds were moderate, and were generally within accepted safe levels.

β -HCH was the most prevalent isomer, implying that hexachlorocyclohexane (HCH) residues were mainly derived from the degradation of technical HCH. The dichlorodiphenyltrichloroethane (DDT) profiles reflected obvious degradation of technical DDT. In the study area, the concentrations of HCBD were <0.02–5.59, 0.03–24.6 ng g⁻¹ dw and 1.65–3.80 ng g⁻¹ lw in soils, plants, and animals, respectively, which were relatively low and not sufficient to cause observable adverse biological effects.

Keywords Organochlorine pesticides · Hexachlorobutadiene · Bioaccumulation · Pesticide factory · Risks

1 Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) have been of increasing concern worldwide because of their persistence, potential for bioaccumulation, and toxicity toward nontarget organisms (Willett et al. 1998; Guo et al. 2014). Although the production and agricultural use of HCHs and DDTs have been banned in many countries, widespread pollution by these OCPs is still occurring in various environmental media and organisms from some countries including China, India and Columbia (Dhananjayan et al. 2011; Liu et al. 2013; Rojas-Squella et al. 2013; Tang et al. 2013; Guo et al. 2014; Pan et al. 2014), and high levels of OCPs in humans and animals have been reported in developing countries in recent years (Qu et al. 2010; Rojas-Squella et al. 2013). Therefore, there is an increasing need to better understand the sources of these chemicals and assess their potential ecological risks.

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From 1952 to 1983, China's total production of HCHs and DDTs was around 4 and 0.27 million tones, respectively (Li et al. 2001; Zhang et al. 2009a, b). In addition, lindane (primarily composed of γ -HCH) and dicofol (contains DDTs) were widely produced in China in the past few years (Qiu et al. 2005; Tao et al. 2005). Extensive and long-term OCP production has resulted in contamination at many industrial sites in China. Previous studies have reported that concentrations of HCHs and DDTs were extraordinarily high in the topsoil from pesticide-producing factories, with a high potential for detrimental biological effects on organisms (Shi et al. 2009; Zhang et al. 2009a, b; Yu et al. 2011; Zhao et al. 2013). However, information regarding soil pollution around pesticide factories is still limited.

Owing to their high lipophilicity and strong resistance to degradation, OCPs are readily accumulated in biological organisms (Pan et al. 2014). Additionally, high concentrations of OCP residues in soils can be volatilized and subsequently enter into vegetation or animals through the air. Moreover, multiclass plants can easily absorb and accumulate OCPs from soils directly, and terrestrial animals may bioaccumulate OCPs through food chains (Dhananjayan et al. 2011; Zhang et al. 2011). As a result, vegetation and terrestrial animals around pesticide factories may be at risks. However, the adverse environmental effects of pesticides in soils are influenced by many factors, such as the OCP levels and interspecific differences in bioaccumulation (Dauwe et al. 2009; Zhao et al. 2013). Investigations of the levels of OCPs existing in terrestrial plants and animals within and surrounding pesticide factories can provide critical information for assessing human and animal health risks.

In this study, a former pesticide-producing factory in Southwest China was selected as a typical OCP-contaminated site and the levels of HCHs and DDTs in soil samples within and around the pesticide factory were measured. In addition, OCPs in terrestrial flora and fauna around the pesticide factory were analyzed to investigate the contamination levels as well as to estimate the effects of point source pollution by OCPs and its potential environmental risks.

Hexachlorobutadiene (HCBd), a chlorinated aliphatic hydrocarbon, has been listed as a candidate persistent organic pollutant by the Stockholm Convention owing to its toxicity, persistence, and potential for bioaccumulation (Tang et al. 2014; Zhang et al. 2014). This molecule is usually generated as a by-product during the production of chlorinated solvents (POPRC 2013). In the study pesticide-producing factory, various chlorinated solvents were produced and used extensively to manufacture other pesticides; HCBd is likely to have been generated unintentionally and released into the environment.

Therefore, the accumulation of HCBd in soils and terrestrial organisms was also investigated around the pesticide factory.

2 Materials and methods

2.1 Study area

The pesticide plant is located in the suburban area of Chongqing in Southwest China and has an enclosed area of 164,000 m². From 1956 to 1983, approximately 220,000 tones of technical HCHs were produced in the factory, while the production of DDTs was estimated to be more than 52,000 tones between 1956 and 1985. Before it was closed in 2008, more than 30 pesticides and intermediate chemicals including organochlorine, organophosphorus and pyrethroids were produced at this facility. The site has been contaminating the surrounding area for decades, and there are currently tens of thousands of people living around the abandoned factory.

2.2 Sample collection

In September 2011, soil samples were collected from sites within and surrounding the former pesticide plant. Within the factory, a total of 12 composite soil samples were collected from 0 to 20 cm below the concrete floors in former pesticide production workshops, warehouses, and offices. Meanwhile, 14 composite surface soil samples (0–20 cm deep) were taken from residential sites, farmlands, and unused lands <1.0 km from the manufacturing facility, using a stainless steel shovel. Composite samples were prepared, consisting of five subsamples from every 100 m² of land. Sampling locations are shown in Fig. 1. Soil samples were placed in a pre-cleaned aluminium box and freeze dried before being ground, homogenized, and stored at –20 °C until analysis.

At the same time, *Zoysia sinica* Hance, $n = 6$), wolfsbane (*Aconitum carmichaeli* Debx, $n = 4$), leaves of other plants including batata (*Ipomoea batatas*, $n = 3$), paper mulberry (*Broussonetia papyrifera*, $n = 3$), carrot (*Daucus carota*, $n = 3$), soybean (*Glycine max*, $n = 4$) and pumpkin (*Cucurbita moschata*, $n = 3$) were collected from the eastern farmland adjacent to the factory (<500 m) using a small stainless shovel. The plant samples were washed with tap water, cut into lengths of <1 cm and mixed well, after which they were freeze dried, ground, homogenized, and stored at –20 °C.

Within a week after the soil sampling, samples of terrestrial fauna, namely, ants (*Polyrhachis vicina* Roger), crickets (*Gryllus testaceus* Walker), grasshoppers (*Acrida chinensis*), locusts (*Oxya chinensis*), free-range chickens

Fig. 1 Map of the sampling sites from the former pesticide producing area, Southwest China

(*Gallus gallusdomesticus*), oriental turtle dove (*Streptopelia orientalis*), great tits (*Parus major*), and red-billed blue magpies (*Urocissa erythrorhyncha*) were collected. Overall, several hundred ants, locusts, grasshoppers, and crickets were collected separately using funnel traps (20 cm diameter). Oriental turtle dove ($n = 3$), great tits ($n = 3$), and blue magpies ($n = 4$) were collected from the eastern farmland using a clapnet. Additionally, a total of five chickens were collected from the villages (<1 km) surrounding the pesticide plant. Complete organisms of the smaller biological samples were obtained. Only the muscle

tissues of chickens and other wild birds were collected. The animal samples were frozen, then thawed and rinsed individually with deionized water to remove impurities. Then all biological samples were freeze dried, ground to a powder, and stored at -20°C until analysis.

2.3 Sample preparation

The soil, plant and terrestrial animal samples were analyzed for pesticides and HCBd using the method described by Tang et al. (2014). Briefly, 10 g of freeze-dried soils or

plant materials was mixed with 30 mL of hexane/dichloromethane (1:1, v/v), then sonicated in an ultrasonic bath for 30 min. The solvent was collected and the procedure was repeated, after which the two extracts were combined and activated copper was added to remove the elemental sulfur. Next, the extracts were concentrated for subsequent cleaning, transferred to a 12-mm i.d. glass column containing 5 cm of alumina and 5 cm of silica gel, and eluted with 70 mL hexane/dichloromethane (7:3, v/v). The eluates were concentrated under a nitrogen stream and diluted to a final volume of 0.5 mL with hexane. Internal standards were added into the extract prior to the analysis by gas chromatography (GC).

The procedure for extraction of the chemicals from the animal samples was the same as that described above, but 5–10 g of each freeze-dried sample was extracted. One aliquot of the extract was used for gravimetric determination of the lipid content, while another was used for chemical analysis after purification on a column containing 5 cm of neutral alumina and 8 cm of neutral silica gel.

2.4 Sample analysis

Organochlorine pesticides and HCBd were identified using an Agilent 7890 gas chromatograph equipped with a Ni^{63} electron capture detector and an Agilent HP-5 column (30 m $\times$ 0.32 mm i.d., film thickness: 0.25 μm). Nitrogen (99.99 % purity) was applied as the carrier gas at 1.0 mL min^{-1} . The injector and detector temperatures were maintained at 250 and 315 $^{\circ}\text{C}$, respectively. The column temperature was programmed as follows: initial temperature of 60 $^{\circ}\text{C}$ for 2 min, followed by an increase to 160 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C min}^{-1}$, then to 210 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$ and finally to 270 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$, where it was held for 3 min. For analysis, 1- μL aliquots of samples were injected in splitless mode.

Total organic carbon (TOC) in soil was measured on a Liqui TOC (Elementar, Germany) at a combustion temperature of 950 $^{\circ}\text{C}$.

2.5 Quality assurance/quality control

All standard solutions were purchased from Supelco (USA). The identities of the target compounds were determined based on comparison with the average retention times of individual authentic standards and confirmed using an Agilent gas chromatograph/mass spectrometer (Agilent 7890 GC/5975 MSD; Agilent Technologies). The average retention times of HCBd, α -HCH, β -HCH, γ -HCH, δ -HCH, *o*, *p'*-DDE, *p*, *p'*-DDE, *o*, *p'*-DDD, *p*, *p'*-DDD, *o*, *p'*-DDT and *p*, *p'*-DDT were at 8.043, 13.597, 14.357, 14.551, 15.259, 20.163, 21.222, 21.512, 22.635, 22.751 and 23.900 min, respectively. 2,4,5,6-tetrachloro-

m-xylene was used as a surrogate standard and pentachloronitrobenzene was used as an internal standard. Procedural blanks and samples spiked with standard mixture were used to monitor the method performance and matrix effects.

The mean spiked HCBd recoveries were 91.6, 78.2, and 82.0 % in the soil, plant, and animal samples, respectively. The mean recoveries of OCP in the soil and organism samples were 74.9–119.4 %. The surrogate standard recoveries in all samples ranged from 76.2 to 81.7 %. The method detection limits (MDLs) were defined as three times the baseline noise. The MDLs for HCBd and the OCPs were 0.02 and 0.01–0.07 ng g^{-1} dry weight, respectively, in each of the matrices. Reported concentrations were not corrected for surrogate recovery in this study.

3 Results and discussion

3.1 OCP residues in soils

The arithmetic means, medians and ranges of the HCH (ΣHCHs , sum of isomers α - + β - + γ - + δ -HCH) and DDT (ΣDDTs = DDT + DDE + DDD) concentrations in the soil samples within and surrounding the pesticide-producing factory are summarized in Table 1. Within the former factory, the concentrations of ΣHCHs and ΣDDTs ranged from 3.89 to 13,386 ng g^{-1} dry weight (dw) and 5.42–11,186 ng g^{-1} dw, respectively. The levels of HCH isomers and DDT-related compounds are also presented in Table 1.

Within the former factory, the average concentrations of ΣHCHs and ΣDDTs were 1854 and 2482 ng g^{-1} of soils, respectively. In the soil samples, the concentrations of ΣHCHs and ΣDDTs varied separately by a factor of about 3000 and 500, indicating uneven distributions of OCPs as a result of the production plants being distributed irregularly at the site. The highest levels of ΣHCHs and ΣDDTs were found in warehouse site, which might be related with past store of pesticide products. In addition, some higher levels of HCHs and DDTs were investigated in the open area of waste equipments, likely reflecting the chemical releases from these waste facilities. HCHs and DDTs exhibited similar contamination levels in this study, which was consistent with their historical production at the site. Previous studies also reported soil pollution with HCHs and DDTs in other former pesticide-producing plants in China (Shi et al. 2009; Zhang et al. 2009a, b; Yu et al. 2011; Zhao et al. 2013). The OCP concentrations in soils from different areas are summarized in Table 2. Although the mean concentrations of OCPs in the soils in the study area were comparable to concentrations found in soils from

Table 1 Concentrations of HCBd, HCHs and DDTs (ng g⁻¹ dw) and total organic carbon (TOC, g kg⁻¹) in the soils within and surrounding the former pesticide producing factory

	Within factory (<i>n</i> = 12)			Surrounding factory (<i>n</i> = 14)		
	Range	Mean	Median	Range	Mean	Median
TOC	3.32–13.5	5.57	5.37	2.35–6.08	4.07	3.61
HCBd	<0.02–5.59	1.45	0.52	<0.02–4.27	0.48	0.07
α -HCH	0.51–2610	446	12.4	11.9–1885	253	38.2
β -HCH	1.84–10,464	1336	86.9	10.5–2854	550	181
γ -HCH	0.50–260	39.9	4.59	0.15–289	45.1	5.77
δ -HCH	1.04–232	32.3	4.78	1.87–1153	102	6.67
<i>o</i> , <i>p</i> '-DDE	0.34–41.7	10.2	2.82	<MDL–14.5	2.19	0.29
<i>p</i> , <i>p</i> '-DDE	5.36–710	184	136	4.35–459	55.6	20.2
<i>o</i> , <i>p</i> '-DDD	0.17–1606	149	13.4	<MDL–491	40.6	3.34
<i>p</i> , <i>p</i> '-DDD	2.63–2819	283	29.6	<MDL–64.9	13.6	5.48
<i>o</i> , <i>p</i> '-DDT	0.18–1976	339	20.4	0.17–99.1	13.4	4.51
<i>p</i> , <i>p</i> '-DDT	3.88–8679	1516	116	0.91–419	87.0	31.8
Σ HCHs	3.89–13,386	1854	93.6	33.8–4926	950	265
Σ DDTs	23.3–11,186	2482	362	5.42–1050	212.3	80.8
α -HCH/ γ -HCH	1.02–18.3	7.47	4.83	1.04–87.5	13.8	6.13
DDT/(DDD + DDE)	0.04–17.8	4.01	1.49	0.05–2.95	1.15	0.91
DDE/(DDD + DDE)	0.14–0.98	0.62	0.68	0.03–1.00	0.67	0.68

DDT including *p*, *p*'-DDT and *o*, *p*'-DDT; DDD including *p*, *p*'-DDD and *o*, *p*'-DDD; DDE including *p*, *p*'-DDE and *o*, *p*'-DDE; MDL, the method detection limit

contaminated sites in Beijing, Yangzhou, and Hangzhou, China (Shi et al. 2009; Zhang et al. 2009a, b; Yu et al. 2011), the maximum concentration of both Σ HCHs and Σ DDTs measured in the present study appeared to be lower. This may have been due to the relatively earlier stoppage of OCP production at this investigated site. However, OCP concentrations in the soils within the contaminated site were 1–3 orders of magnitude higher than those found in soils from other agricultural fields and urban areas, suggesting that this abandoned industrial site was heavily contaminated with HCHs and DDTs (Table 2).

The concentrations of Σ HCHs and Σ DDTs in the soils around the abandoned factory were lower than those observed in soils within the factory (Table 1). As expected, the levels of OCPs in the soils surrounding the pesticide factory were 1–2 orders of magnitude higher than those found in the agricultural soils from the Haihe Plain, Yangtze River Delta, and Pearl River Delta in China (Gao et al. 2008; Tao et al. 2008; Zhang et al. 2009a, b). The OCP levels were comparable to concentrations found in soils from paddy fields with high amounts of HCH and DDT residues in Northeast India (Mishra et al. 2012). The data reported here suggest that the surface soils surrounding the former pesticide factory have been subjected to relatively high levels of OCP pollution. Relatively levels of HCHs and DDTs were found in the sites located the south of factory, which maybe reflected the effects of the dominant wind direction. Another main impact factor of the

investigated OCPs appeared to be soil organic carbon ($p < 0.05$), which had a positive influence on DDTs and HCHs. Nevertheless, the highest TOC-normalized concentrations were not observed at sites nearest to the production plant. Similar results have been reported for soils around a pesticide factory in Zibo, China (Zhao et al. 2013). Overall, these findings indicate that the migration and distribution of OCPs in soil is a complex process affected by many factors.

Four HCH isomers were detected in the soil within and around the abandoned pesticide factory. Within the former factory, the average composition of HCH isomers in the soil samples was α -HCH: 21.4 %, β -HCH: 67.7 %, γ -HCH: 5.11 %, and δ -HCH: 5.76 %. Technical-grade HCH is usually a mixture of α -HCH (71 %), β -HCH (6 %), γ -HCH (14 %), and δ -HCH (9 %) in China (Lin 1996), with β -HCH being the isomer that is most stable and readily accumulated in soil (Walker et al. 1999). Moreover, the isomers of α -HCH and γ -HCH can be transformed into β -HCH in the environment (Walker et al. 1999; Li et al. 2001). The high percentage of β -HCH implied that technical HCH production had been stopped for many years (Zhao et al. 2013). A similar composition of HCH isomers (β -HCH representing 78.3 % of the Σ HCHs) was measured in the soils surrounding the factory. The ratio of α -HCH/ γ -HCH is often used as an indicator of recent γ -HCH input into the environment (Abhilash and Singh 2008). In the present study, most of the ratios of α to γ -HCH within the

Table 2 Concentrations of organochlorines (ng g^{-1} dw) in soil samples from this former pesticide producing area and from other areas

Regions	Site types	Sampling times	ΣHCHs	ΣDDTs	References
Beijing, China	Within former OCP producing factory	2005	168–103,254 (1958)	114–466,100 (3998)	Shi et al. (2009)
Yangzhou, China	Around gate of OCP producing factory	2008	313	33,748	Zhang et al. (2009a, b)
Hangzhou, China	Within former OCP producing factory	2009	2.60–80,130 (1614)	<MDL–49,180 (1742)	Yu et al. (2011)
Chongqing, China	Within former OCP producing factory	2011	3.89–13,386 (1854)	23.3–11,186 (2482)	The present study
Zibo, China	Around OCP producing factory		248–42,838	775–226,711	Zhao et al. (2013)
Haihe plain, China	Agricultural soils	2004	0.02–349 (3.90)	0.40–2350 (64)	Tao et al. (2008)
Yangtze River Delta, China	Agricultural soils	2003	0.28–17.9 (3.23)	0.46–484 (28.9)	Zhang et al. (2009a, b)
Guangzhou, China	Agricultural soils	2004	0.20–104 (4.40)	7.60–663 (67.3)	Gao et al. (2008)
Southeast China	Urban/rural/background soils	2011	0.41–6.78 (2.44)	1.77–25.03 (11.36)	Yang et al. (2013)
North-East India	Agricultural fields/fallow/urban land	2009–2010	98.0–1945 (825)	166–2288 (903)	Mishra et al. (2012)
SE Romania	Industrial and agricultural sites	2009	6.00–6818	27.0–5826	Ene et al. (2012)
Chongqing, China	Around former OCP producing factory	2011	33.8–4926 (950)	5.42–1050 (212)	The present study

Values are presented as range and/or mean (given in parentheses)
MDL the method detection limit

factory, ranged from 3 to 7 indicating that they were primarily derived from historical production of technical HCH. Additionally, some of the ratios were found to be >7 in soils surrounding the factory. This finding is reasonable since γ -HCH is less stable than α -HCH and can isomerize to α -HCH, which would cause the ratio to increase gradually after long-term contamination by technical HCH (Willett et al. 1998).

The composition of DDTs was similar within and around the pesticide factory. *p*, *p'*-DDT dominated the DDT-related compounds, with a mean of 45.5 and 59.3 % in the soil samples within and around the former factory, respectively. This was followed by *p*, *p'*-DDE, which had corresponding abundances of 26.4 and 14.6 %. In most samples, the levels of *p*, *p'*-DDT were much higher than those of *o*, *p'*-DDT, which is consistent with the technical DDT composition. Generally, technical DDT contains 77.1 % *p*, *p'*-DDT, 14.9 % *o*, *p'*-DDT, 4 % *p*, *p'*-DDE, and <5 % others (Bopp 1982; Zhu et al. 2005). The ratio of DDT/(DDD + DDE) with a reference value of 1.0 can be used to assess the application time of DDT (Tao et al. 2008). Samples with ratios of DDT/(DDD + DDE) >1 were found in most of the sites studied (Table 1), further demonstrating the historical contamination with technical DDT. DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions (Aislabie et al. 1997). In this study, most values of the DDE/(DDD + DDE) ratio exceeded 0.5, indicating that DDT degradation had happened largely under aerobic conditions in the soils.

3.2 OCP pollution in plants

The OCP contents in plants surrounding the abandoned pesticide factory are presented in Fig. 2. Residues of OCPs in plants ranged from 21.5 to 328 ng g^{-1} dw for ΣHCHs and 26.5–484 ng g^{-1} dw for ΣDDTs . Consistent with the results observed for the soil samples, the concentration of ΣDDTs was comparable to that of ΣHCHs in plants. However, large interspecies differences were observed in the OCP concentrations of plants, and all chemicals were found at higher concentrations in wolfsbane than in other species, indicating different OCP accumulative capacities. There is currently little information available regarding OCP concentrations in plants around other former pesticide factories, however, contamination with OCPs has been reported in various plants, including vegetables, grass, and trees from farms and industrial regions (Wang et al. 2007; Lin et al. 2008; Pan et al. 2014). Inconsistencies in species, growth, and development of plants have made it difficult to draw comparisons, so simple comparisons were made using the levels of ΣHCHs and ΣDDTs when possible. The OCP concentrations found in plants from different regions

Fig. 2 Levels of organochlorine pesticides and hexachlorobutadiene in plants (a) and terrestrial animals (b) from the former pesticide producing area, Southwest China. The bars indicate the standard deviations

are shown in Table 3. In general, the concentrations of both HCHs and DDTs in plants were one order of magnitude higher in the present contaminated site than in other areas (Wang et al. 2007; Lin et al. 2008; Yi et al. 2012; Tarcau et al. 2013; Pan et al. 2014). These findings confirm that the contaminated sites are significant sources of pollution if left untreated, resulting in local and regional plant contamination.

As shown in Fig. 3a, the β -HCH ranged from 13.9 to 62.0 % in the seven plant species, with a mean of 37.9 %. The accumulation of β -HCH in plant samples implies that HCH residues are primarily derived from the former pesticide factory. Notably, the ratio of α -HCH/ γ -HCH in some plants was less than the ratio of 3–7 found in technical HCH (Fig. 3a). However, pure lindane was never produced in this former factory; therefore, the relatively lower ratios of α -HCH/ γ -HCH might be related to differential accumulation or metabolism of HCH isomers in plants rather than fresh input of γ -HCH. Larger interspecies differences in the ratios of α -HCH/ γ -HCH were reported for agricultural crops from an intensive horticultural area in Hohhot, China (Wang et al. 2007). The profiles of DDT-related

compounds in plants are presented in Fig. 4a. When compared with soil samples, an inversion between the dominance of DDT in favor of DDD was observed in the plant samples. DDD (p, p' -DDD and o, p' -DDT) was present at percentages higher than 47.7 % of ΣDDTs . The ratios of (DDD + DDE)/DDT ranged from 1.27 to 6.10, with a mean of 3.51 (Fig. 2a). The DDT metabolites were more prevalent than the parent materials, suggesting either efficient biotransformation of the parent materials in the plant systems or old sources of DDT contamination. In general, the DDD/(DDD + DDE) ratios were >0.5 , indicating that the biodegradation of DDT was anaerobic. As shown in Fig. 2a, the p, p' -DDT/ o, p' -DDT ratio (mean = 2.19) suggests that the DDTs in the plants were mainly derived from the technical DDT emissions from the former pesticide factory.

3.3 Accumulation of OCPs in terrestrial fauna

The HCHs and DDTs measured in various terrestrial animal samples are listed in Fig. 2b. The lipid normalized

Table 3 Concentrations of organochlorine pesticides in terrestrial plants (ng g^{-1} dry weigh) and animals (ng g^{-1} wet weigh) from this former pesticide producing area and from other areas

Species	Regions	Sampling times	ΣHCHs	ΣDDTs	References
Plants					
Grass	Farms, Sichuan, China	2011	0.82–2.45 (1.38)	1.60–6.00 (2.88)	Pan et al. (2014)
Mosses	Forest, North-Eastern Romania	2005	8.90–130	5.80–95.0	Tarcau et al. (2013)
Grass	Farms, Mt. Qomolangma, China	2005	0.35–7.82	1.53–9.46	Wang et al. (2007)
9 tree leaves	Industrial region, Sichuan, China	2006	(48.3)	(124)	Lin et al. (2008)
15 herbage	Industrial region, Sichuan, China	2006	(27.2)	(20.1)	Lin et al. (2008)
10 vegetables	Industrial region, Sichuan, China	2006	(37.5)	(9.77)	Lin et al. (2008)
Tea leaves	Farms, Fujian, China	2009	0.37–7.43 (2.80)	0.12–5.17 (2.50)	Yi et al. (2012)
Grass, vegetables and tree leaves	Around former OCP producing factory, Chongqing, China	2011	21.1–327 (84.1)	26.5–533 (126)	The present study
Animals					
Chicken muscle	Poultry farm, Beijing, China	2006	(6.96) L	(15.8) L	Tao et al. (2009)
Slaty-breasted rail	E-waste recycling region, Guangdong, China	2005–2007	4.40–14.0 (7.90)	7.40–11.0 (8.70)	Zhang et al. (2011)
Common moorhen	E-waste recycling region, Guangdong, China	2005–2007	(1.90)	(9.30)	Zhang et al. (2011)
Oriental turtle dove	E-waste recycling region, Guangdong, China	2005–2007	2.50–6.60	1.60–1.80	Zhang et al. (2011)
House sparrow	Forests, Tamil Nadu, India	2001–2006	10.0–270 (40.0)	<MDL–400 (60.0)	Dhananjayan et al. (2011)
Chicken and birds	Around former OCP producing factory, Chongqing, China	2011	83.5–280 (140) L	9.29–30.9 (22.3) L	The present study

Values are presented as range and/or mean (given in parentheses)

MDL the method detection limit, L ng g^{-1} lipid weigh

Fig. 3 The composition of HCHs in the plants (a) and terrestrial animals (b) from the former pesticide producing area, Southwest China

residues ranged from 9.81 to 280 ng g⁻¹ lipid weight (lw) for ΣHCHs, and from 9.29 to 407 ng g⁻¹ lw for ΣDDTs.

OCP levels in insects differed among species: ant > cricket > locusts > grasshoppers. The interspecies differences in OCP accumulation may be due to diet and habitat. In the four insects investigated, the proportion of β-HCH ranged from 38.1 to 44.6 %, with an average of 39.5 %. β-HCH was the most prevalent isomer in insects, probably due to its greater resistance to enzymatic degradation, lipophilicity, and its bioaccumulation potential (Tanabe et al. 1998). ΣDDT concentrations in the insects ranged from 32.6 to 407 ng g⁻¹ lw, with a mean value of 146 ng g⁻¹ lw. To the best of our knowledge, no previous studies have investigated OCP residues in nontarget terrestrial insects in a natural environment. As shown in Fig. 2b, higher DDT accumulation in insects might be attributed to frequently elevated exposure to heavily polluted soils in this area. Among the individual DDT analogs, *p*, *p'*-DDD was the predominant congener in the insects, contributing an average of 31.2 % of the ΣDDT, followed by *p*, *p'*-DDT (18.0 %). The ratios of (DDD + DDE)/DDT were much higher than 1.0, and the concentrations of DDD were greater than those of DDE (Fig. 2b). The high levels of *p*, *p'*-DDD found in our study may be linked to the

anaerobic degradation of DDT and direct exposure to DDD via food chains.

The OCP residues were also measured in muscle samples from free-range chickens and wild birds. The mean residuals of HCHs and DDTs in chicken (lipid content, 0.70 %) were 85.6 and 23.1 ng g⁻¹ lw, respectively. Tao et al. (2009) reported that the mean lipid weight concentrations of HCHs and DDTs were 6.96 and 15.8 ng g⁻¹ lw, in chicken muscle samples collected from a poultry farm in Beijing in 2006, which are substantially lower than those observed in the present study. Levels of OCP residuals in chicken muscle measured in this study were higher than those recently reported for samples from 13 Chinese markets, where DDTs were detected in only 42.3 % of total samples and HCHs were quantifiable in <40 % of the samples (Zhou et al. 2010). In the study area, OCP concentrations in the oriental turtle dove, great tits, and blue magpies were in the same order of magnitude (Fig. 2a). Data for OCP concentrations in these three birds from other areas are scarce; however, as shown in Table 3, the OCP concentrations in the birds in this study were comparable to those in omnivorous birds from other regions (Dhananjayan et al. 2011; Zhang et al. 2011). Conversely, the OCP levels in these studied birds were lower than those reported

Fig. 4 The composition of DDTs in the plants (a) and terrestrial animals (b) from the former pesticide producing area, Southwest China

in house sparrows from Tamil Nadu, India (Dhananjayan et al. 2011). The consistent levels of contamination in birds observed in this study are understandable since the birds are all migratory species. Dietary composition and metabolic capacity of pollutants may also affect OCP accumulation in birds.

Figures 3b and 4b show the compositions of HCHs and DDTs measured in chickens and other birds. β -HCH was the predominant isomer in the biological samples, contributing an average of 88.3 % of the Σ HCHs. p, p' -DDT dominated the DDT-related compounds. The composition profiles of both HCHs and DDTs of chickens and birds differed from those of plants in the area (Figs. 3, 4). Although ingestion was the dominant exposure pathway of chickens and birds to OCPs, the variations in metabolic rates of different chemicals likely resulted in the difference in composition profiles, which was demonstrated by the difference in composition profiles between feed and droppings of chickens in a previous study (Tao et al. 2009). HCHs are largely represented by β -HCH because of the relatively higher metabolic rate of α -HCH and greater persistence of β -HCH. The ratios of (DDD + DDE)/DDT were >1.0 in all samples from the chickens and wild birds, indicating that the technical DDT was further degraded in

these species or their feedstuffs. The higher levels of DDD compared to DDE found in our study may be associated with anaerobic degradation of DDT or direct exposure to DDD via food chains.

3.4 Levels and distribution of HCBd

The HCBd concentrations ranged from <0.02 to $5.59 \text{ ng g}^{-1} \text{ dw}$ in the soil samples (Table 1). Although the mean HCBd concentrations in soils from within the pesticide factory were higher than from the surrounding areas, this difference was not significant ($p = 0.136$). The TOC content of soil significantly affected the distribution of HCBd ($r = 0.483$, $p < 0.05$). Surprisingly, the HCBd level in soils was not high in the study area. Tang et al. (2014) found HCBd concentrations between <0.02 and $3.10 \text{ ng g}^{-1} \text{ dw}$ in soils from an agricultural area in East China and Zhang et al. (2014) reported that the concentrations in soil around a pesticide plant had a range of 0.04 – $3.33 \text{ ng g}^{-1} \text{ dw}$. The HCBd concentrations in soils in this study were much lower than those reported in soils from plants producing perchloroethylene and trichloroethylene in the United States (USEPA 1976). Compared with those areas, the surface soils within and around

the abandoned pesticide factory have rather low levels of HCBd pollution. There are few data available regarding the persistence of HCBd in soils. Environment Canada (1999) and Taylor et al. (2003) reported that HCBd may not degrade in soil under anaerobic conditions. However, Bosma et al. (1994) found the removal of HCBd under anaerobic conditions after 4 months of acclimation, but no removal over 3 years under aerobic, non-reductive conditions. It is difficult to differentiate the historical HCBd emissions from those associated with the former factory since the levels of the main degradation product from HCBd in soils were not analyzed in this study.

As shown in Fig. 2a, the HCBd concentrations in the seven plants analyzed were 0.03–24.6 ng g⁻¹ dw (mean = 7.33 ng g⁻¹). Large interspecies differences were observed in the HCBd content of the plants, with the highest concentration being found in the leaves of paper mulberry, followed by those of zoysia. Only a few studies of HCBd residues in terrestrial plants have been published to date. Grapes from the United Kingdom reportedly contained 3.7 ng g⁻¹ of HCBd (McConnell et al. 1975), and Tang et al. (2014) found HCBd concentrations of 0.8–2.0 ng g⁻¹ dw in six plants from an agricultural area in China. In a previous study, HCBd was found to be strongly bioaccumulated by rice and vegetables, even though low HCBd concentrations were observed in the soil they grew in (Tang et al. 2014). The results of the present study further confirm the strong potential for HCBd to become concentrated in plants.

Hexachlorobutadiene concentrations of 1.65–3.80 ng g⁻¹ lw were found in the terrestrial animals (Fig. 2b). In contrast to the plant samples, only small interspecies differences were observed in the HCBd concentrations in the animals. Tang et al. (2014) found HCBd concentrations of 1.30–8.20 ng g⁻¹ lw in terrestrial animals from a farm in China, while HCBd concentrations ranging from below the detection limit to 4.90 ng g⁻¹ lw were observed in terrestrial animals from Greenland (Vorkamp et al. 2004). However, higher HCBd concentrations (5.7–13.7 ng g⁻¹ wet weight) were found in human liver samples, which was likely due to hepatic metabolism of HCBd (IPCS 1994). The low HCBd concentrations in the animals investigated here might be related to the low level of HCBd pollution in soils and plants in this area. Furthermore, HCBd was found to be removed from animals within 72 h via urine and feces in a study employing radiolabeled HCBd (IPCS 1994). This rapid depuration rate might play an important role in the low levels of HCBd in animals.

3.5 Potential ecological risks

The potential risk of OCPs in soil was evaluated according to soil-quality guidelines. Soil concentrations of DDT in

one third of the investigated sites, and of HCHs in almost all the sites studied exceeded the Romanian soil regulatory levels (alert level in the agricultural/residential area: Σ DDTs, 500 ng g⁻¹; α -HCH, 100 ng g⁻¹; β -HCH, 50 ng g⁻¹; γ -HCH, 20 ng g⁻¹), respectively, implying wide soil pollution in the studied area (Ene et al. 2012). Within the former pesticide factory, one third of the sites had HCH and DDT levels far greater than the guideline values (industrial soils: Σ HCHs, 4000 ng g⁻¹; Σ DDTs, 1700 ng g⁻¹) based on China's first nationwide survey of soil pollution (MEP 2008) and the Dutch soil intervention values of DDTs (DDT, 1700 ng g⁻¹; DDE, 2300 ng g⁻¹) and HCHs (β -HCH, 1600 ng g⁻¹; γ -HCH, 1200 ng g⁻¹) (VROM 2009). These findings indicate that there is a high-level risk of pollution in the former OCP factory region and that on-site remediation technologies are needed to eliminate OCP contamination. OCP levels exceeding the allowed concentrations were observed in most of the soils collected from the area surrounding the abandoned factory based on China's environmental quality evaluation standard for farmland used to cultivate edible agricultural products (HJ/T 332–2006; Σ HCHs, 100 ng g⁻¹; Σ DDTs, 100 ng g⁻¹). The levels of OCPs were also above the limit for contaminants in residential sites of the Canadian Environmental Quality Guidelines (CCME 2007) in some soil samples surrounding the former factory, implying that land in this area would only be suitable for residential purposes if effective soil remediation was conducted. Based on these results, we conclude that heavy soil pollution has occurred in the study area, which may have caused long-term eco-toxicological damage within and around the abandoned pesticide factory.

The OCP levels in some of the plant samples exceeded the limits set by the European Commission (2006), which specifies γ -HCH, *o*, *p*'-DDE, *p*, *p*'-DDE, *o*, *p*'-DDD, *o*, *p*'-DDT, and *p*, *p*'-DDT limits of 10, 50, 50, 50, 50, and 50 ng g⁻¹, respectively, for some edible leaf vegetables and feed of plant origin. In the present study, the HCH and DDT levels in four of the plants exceeded the maximum residue limits (MRLs) for pesticides in China's food safety standard (GB 2763–2012; leaf vegetables: Σ HCHs, 50 ng g⁻¹; Σ DDTs, 50 ng g⁻¹). These comparisons suggest that moderate OCP pollution is present in plants in the region, indicating the potential for negative impacts on human and animal health through food chains.

The OCP levels in chickens did not exceed the maximum residue limits for pesticides in China's food safety standard (Σ HCHs, 100 ng g⁻¹; Σ DDTs, 200 ng g⁻¹), or the FAO/WHO's maximum residue limits (γ -HCH, 100 ng g⁻¹ fat, Σ DDTs, 5000 ng g⁻¹ fat) (FAO/WHO 2004), indicating that the consumption of chickens would not pose an immediate risk to local residents. The average concentrations of *p*, *p*'-DDE of 20–1000 μ g g⁻¹ lw in the

liver of birds pose a threat to individual bird reproduction and therefore the overall population (Tanabe et al. 1998). No avian toxicity reference value is available for HCHs, but the hatch ability of ring-necked pheasants and American kestrel eggs was not affected by concentrations of β -HCH and γ -HCH as high as 10 and 5.5 $\mu\text{g g}^{-1}$ ww, respectively (Wiemeyer 1996). Owing to the much lower levels of HCHs and DDTs observed in the muscles of birds, current OCP concentrations would not likely cause adverse effects on the reproduction of avian species in the study area. However, it should be noted that OCP concentrations were not determined in the livers and eggs of birds in the present study. To the best of our knowledge, no investigations of the toxicological levels of OCPs in terrestrial nontarget insects have been conducted to date. Greater attention should be given to the possible harmful impacts of the accumulated OCPs in terrestrial insects.

The HCBd concentrations detected in all soil samples were below the guideline value (1.0 $\mu\text{g g}^{-1}$) for uncontaminated soils set by the Chinese standard for soil-quality assessment for exhibition sites (SEPA 2007), as well as the concentration limits of 6.7 and 10.0 ng g^{-1} for agricultural coarse- and fine-grained soils, respectively, recommended in the environmental quality standard draft for Saskatchewan, Canada (Saskatchewan Ministry of Environment 2011). These findings indicate that only low-level HCBd pollution was present in soils from the contaminated site. The HCBd concentrations in animals analyzed in this study were lower than those reported in several previous studies (Gabrielsen et al. 2004; POPRC 2013; Tang et al. 2014), and much lower than the concentrations given in an HCBd hazard assessment for animals (POPRC 2013); accordingly, the levels in the study area are probably insufficient to cause observable adverse effects on wildlife.

4 Conclusion

This study clearly demonstrated that the former pesticide-producing site and its surrounding area have been seriously contaminated by OCPs. Effective soil remediation is needed within the former factory to eliminate OCP contamination from the soils. Additionally, the high concentrations of HCHs and DDTs in soils revealed that there could be eco-toxicological damage around the factory. As expected, higher levels of OCPs were found in plants from the surrounding areas of the point sources; accordingly, these compounds have the potential to induce adverse biological effects in humans and other animals. In this investigation, moderate levels of OCP pollution were also observed in terrestrial insects, free-range chickens or birds from the former pesticide-producing area. HCBd was found to be widely distributed in soils, plants, and terrestrial fauna, but

HCBd residues were generally within safe levels in the study area. Given the potential risk of these chemicals to wildlife and human health, continual monitoring and environmental and health risk assessments are needed in this region.

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