



Occurrence of Organochlorine Pesticides in Farmland Soils of Xi'an, China

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In this study, 25 representative farmland soil samples from suburban areas in Xi'an, the capital city of Shaanxi province, China, were collected and analyzed for 20 organochlorine pesticides (OCPs). The concentrations were in the ranges of 0.22-11.24 ng g⁻¹ for HCHs (sum of α , β , γ and δ -HCH, avg. 3.56 ng g⁻¹), 0.76-56.30 ng g⁻¹ for DDTs (sum of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, avg. 12.80 ng g⁻¹), 0.47-12.95 ng g⁻¹ for CHLs (sum of heptachlor, heptachlor epoxide isomer B, α -chlordane and γ -chlordane, avg. 5.90 ng g⁻¹), 0.64-31.51 ng g⁻¹ for other organochlorine pesticides (sum of aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone and methoxychlor, avg. 11.89 ng g⁻¹). HCHs, DDTs and CHLs were the most dominant compounds among the 20 organochlorine pesticides. Source identification analysis indicated that the residues of HCHs, DDTs and CHLs were mostly due to historical use of these chemicals or from other source regions. The quality of Xi'an farmland soil was classified as low pollution by organochlorine pesticides according to the national environmental quality standards for soils of China (GB15618-1995).

Key Words: Farmland soil, Organochlorine pesticides, Xi'an, Residue.

INTRODUCTION

Organochlorine pesticides (OCPs) are a typical class of persistent organic pollutants (POPs) and have been of great concern around the world because of their high lipophilicity, persistence, long-range transportation and toxic biological effects in the environment¹⁻³. These OCPs, including heptachlor, aldrin, endosulfan, dieldrin, endrin, endrin aldehyde, endrin ketone, methoxychlor, endosulfan sulfate and heptachlor epoxide, dichlorodiphenyltrichloroethane (DDT) and their metabolites, had been widely produced and used in agriculture and sanitation for several decades^{4,5}. Although these OCPs had been restricted in several countries including China since 1980s, notably high levels of OCPs in recent years have still been detected in some different environmental samples and may continuously induce a significant impact on the environment and ecosystems⁶⁻¹².

The Loess Plateau, one of the most important food-growing agriculture areas in China, covered an area of some 640,000 km² with a population of more than 50 million and has a long history of OCPs usage and production for pest controls. However, very few studies have been published on residues of OCPs in the Loess Plateau to our knowledge. Of all metropolis located in the Loess Plateau, Xi'an, a world famous tourist city and an inexhaustible treasure house of cultural relics, is located in the south of the Loess Plateau, where OCPs were

extensively used from the 1950-1980 s. Information collected will provide a better understanding of OCPs pollution in this area and is truly indispensable for decision-makers to take effective measures to minimize potential health and ecological risk³. The purpose of this study was to determine the residue levels of 20 OCPs and to examine the possible sources of these OCPs in farmland soils of Xi'an in the Loess Plateau of China.

EXPERIMENTAL

Sample collection and extraction: Farmland soil samples (depth 0-10 cm) from 25 sampling sites were collected around Xi'an in summer, 2012 (Fig. 1). During the sample collection, a global positioning system was used to locate the sampling sites. After sampling, all samples were transported to the laboratory, freeze dried and homogenized using a mortar and pestle. The extraction of soils samples was carried out using an accelerated solvent extractor (Dionex ASE 350). The sample (10 g) was flushed by DCM:hexane (2:3, v/v) at 100 °C and 7.6 × 10⁶ Pa (3 times, 5 min interval each), then the extract was concentrated under a gentle N₂ stream and purified by column chromatography (30 cm × 1 cm i.d.) using Florisil (4 g) as adsorbent. The column was eluted with 60 mL of DCM:hexane (3:7, V/V) for the collection of the OCP fraction, then concentrated and solvent-exchanged to hexane and reduced to 0.5 mL under a gentle stream of nitrogen before analysis.

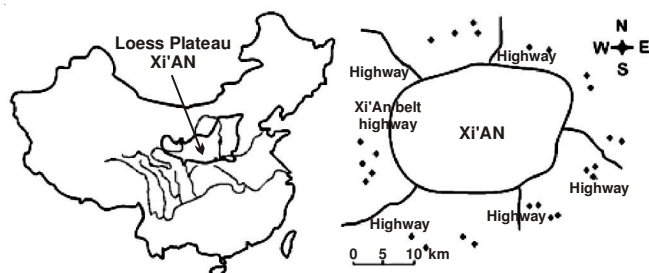


Fig. 1. Sketch map of the study area and sampling locations

Instrumental analysis: All sample extracts were analyzed with a HP6890 gas chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD). A HP-5 (30 m \times 0.25 mm i.d. with 0.25 mm film thickness) capillary column was used for separating the target analytes. Nitrogen was used as the carrier gas at 2.5 mL/min under the constant flow mode. Injector and detector temperatures were maintained at 290 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. Column temperature was programmed from 60 $^{\circ}\text{C}$ (held for 2 min) to 150 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$, followed by a ramp to 210 $^{\circ}\text{C}$ at a rate of 2 $^{\circ}\text{C min}^{-1}$, to 290 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ (held for 10 min). Injection was conducted in splitless mode.

Quality control and quality assurance (QC/QA): A mixture of 20 OCP standard (including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p' -DDT, p,p' -DDD, p,p' -DDE, heptachlor, heptachlor epoxide isomer B, α -chlordane, γ -chlordane, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone and methoxychlor), surrogate standard (PCB191) and internal standard (PCNB) were all purchased from o2si Smart Solutions (USA). The surrogate was added to each sample to monitor procedural performance and matrix effects. Quantification was performed by five-point calibration method (from 1-500 ng mL $^{-1}$, $r^2 >$

0.995). The reporting limit was defined as the lowest concentration level from the calibration curve for a specific analyte. For each batch of 10 field samples, a procedural blank, a spiked blank, a pair of spiked matrix sample/duplicate and a sample replicate were processed. The recoveries of the surrogate standards from all samples and blanks were 75-121 % and the variation of OCPs in duplicate samples was less than 20 %.

RESULTS AND DISCUSSION

Concentration of organochlorine pesticides in soils:

The mean, minimum, maximum concentration and number of detected samples of 20 OCPs in Xi'an farmland soil were shown in Table-1. Most of OCPs were detected in soil samples except for endosulfan sulfate, endrin aldehyde and methoxychlor, which were not discussed later. Among these OCPs, HCHs, DDTs and CHLs were the most dominant compounds. The total concentration of tested pesticides ranged in 4.10-83.49 ng g $^{-1}$ with a mean value of 34.91 ng g $^{-1}$.

DDTs were found in all soil samples. The total concentrations of DDTs (sum of p,p' -DDT, p,p' -DDD and p,p' -DDE) ranged from 0.76 to 56.30 ng g $^{-1}$ with a mean value of 12.80 ng g $^{-1}$. Among DDT and its metabolites, p,p' -DDE was the most abundant and its concentrations varied from 0.46-42.54 ng g $^{-1}$ with a mean value of 6.86 ng g $^{-1}$. p,p' -DDT was the second highest, varying from n.d. to 14 ng g $^{-1}$ with an average value of 4.17 ng g $^{-1}$. p,p' -DDD was the third highest, ranged from n.d. to 6.66 ng g $^{-1}$ with a mean value of 1.77 ng g $^{-1}$. Compared to other regions and countries, DDT contamination in farmland soil of Xi'an was lower than those in similar agricultural areas in China such as Shanghai³, Haining⁶, Hong Kong⁷, Guangzhou¹⁰, Beijing¹², Shenyang¹³ and in Poland (4.3-2400 ng g $^{-1}$)¹⁴ and German (23.7-173 ng g $^{-1}$)¹⁵. The relatively lower level of DDTs indicated a decreasing trend in farmland soil DDT contamination of Xi'an.

TABLE-1
CONCENTRATION (ng g $^{-1}$) OF INDIVIDUAL OCPs IN FARMLAND SOIL OF XI'AN

Compound	Number of detected	Minimum	Maximum	s.d.	Mean
p,p' -DDE	25	0.46	42.54	9.10	6.86
p,p' -DDD	21	n.d.	6.66	1.76	1.77
p,p' -DDT	24	n.d.	14.00	3.94	4.17
DDTs	—	0.76	56.30	13.38	12.80
α -HCH	25	0.22	2.57	0.50	0.72
β -HCH	18	n.d.	6.22	1.43	2.02
γ -HCH	18	n.d.	2.13	0.47	0.56
δ -HCH	15	n.d.	0.76	0.26	0.25
HCHs	—	0.22	11.24	2.43	3.56
Heptachlor	22	n.d.	4.04	1.04	1.19
Heptachlor epoxide isomer B	21	n.d.	3.44	0.96	0.80
α -Chlordane	25	0.29	6.84	1.38	2.14
γ -Chlordane	25	0.18	4.41	1.07	1.78
CHLs	—	0.47	12.95	3.55	5.90
Endosulfan I	23	n.d.	4.89	1.32	1.60
Endosulfan II	19	n.d.	8.50	2.54	2.23
Endosulfan sulfate	0	n.d.	n.d.	—	—
Aldrin	25	0.20	3.44	0.96	0.80
Dieldrin	19	n.d.	4.56	1.29	1.00
Endrin	23	n.d.	13.35	3.25	3.58
Endrin aldehyde	0	n.d.	n.d.	—	n.d.
Endrin ketone	19	n.d.	9.57	2.28	2.10
Methoxychlor	0	n.d.	n.d.	—	—

HCHs, another typical OCPs including α -HCH, β -HCH, γ -HCH and δ -HCH, were all detected in Xi'an farmland soil. The total concentrations of HCHs (sum of α -HCH, β -HCH, γ -HCH and δ -HCH) varied from 0.22 to 11.24 ng g⁻¹ with an average value of 3.56 ng g⁻¹. Among them, the concentration of individual chemical was generally in an order: β -HCH > α -HCH > γ -HCH > δ -HCH. β -HCH was the most dominant, which ranged from n.d. to 6.22 ng g⁻¹ with a mean value of 2.02 ng g⁻¹. The concentrations of α -HCH, γ -HCH and δ -HCH ranged from 0.22-2.57 ng g⁻¹ (avg. 0.72 ng g⁻¹), n.d. to 2.13 ng g⁻¹ (avg. 0.56 ng g⁻¹), n.d. to 0.76 ng g⁻¹ (avg. 0.25 ng g⁻¹), respectively (Table-1). Compared to other regions in China, e.g. Shanghai (2.4 ng g⁻¹)³, Beijing (1.5 ng g⁻¹)⁹, Haining (0.7 ng g⁻¹)⁶, Harbin (7.1 ng g⁻¹)¹¹, Guangzhou (6.2 ng g⁻¹)¹⁰ and Hong Kong (6.2 ng g⁻¹)⁷, the contamination of HCHs in farmland soil of Xi'an was found in a medium level (Table-2).

Heptachlor, heptachlor epoxide isomer B, α -chlordane and γ -chlordane are the most abundant chlordane-related compounds (CHLs) and are still being used against termites in China nowadays¹⁶. The total concentrations of CHLs (sum of heptachlor, heptachlor epoxide isomer B, α -chlordane and γ -chlordane) varied from 0.47-12.95 ng g⁻¹ with an average value of 5.90 ng g⁻¹. The levels of CHLs found in this study were higher than those in agricultural soil of Shanghai (from n.d. to 10.0 ng g⁻¹, avg. 2.5 ng g⁻¹)³. Among them, α -chlordane and γ -chlordane were detected in all soil samples and ranged from 0.29-6.84 ng g⁻¹ (avg. 2.14 ng g⁻¹), 0.18-4.41 ng g⁻¹ (avg. 1.78 ng g⁻¹), respectively (Table-1) and Heptachlor, heptachlor epoxide isomer B were detected in 22 and 21 of the 25 samples and ranged from n.d. to 4.04 ng g⁻¹ (avg. 1.19 ng g⁻¹), n.d. to 3.44 ng g⁻¹ (avg. 0.80 ng g⁻¹), respectively (Table-1).

The other OCPs, including endosulfan I, endosulfan II, aldrin, dieldrin, endrin and endrin ketone, were also found in farmland soil of Xi'an. Their total concentrations were in the range of 0.64-31.51 ng g⁻¹ with a mean value of 11.89 ng g⁻¹. Among them, endosulfan I and endosulfan II are still being used on cotton and crops in China. In our study, the total concentrations of endosulfan (sum of endosulfan I and endosulfan II) varied from n.d. to 12.60 ng g⁻¹ (avg. 3.83 ng g⁻¹). The concentration of endosulfan II (avg. 2.23 ng g⁻¹) was slight higher than that of endosulfan I (avg. 1.60 ng g⁻¹) probably because of the more rapid degradation of endosulfan I. Aldrin, dieldrin, endrin and endrin ketone had never been produced and farmland used in China, however, these chemical were also detected in farmland soils of Xi'an with a relatively high

level ranging from 0.33-18.92 ng g⁻¹ (avg. 8.06 ng g⁻¹). The high contamination level of these OCPs was possibly transported by air parcels since they were detected in PM_{2.5} and PM₁₀ in Beijing¹⁷ and other water samples¹⁸.

Sources and fate of DDT, HCH and chlordane: The relationships between the parent compounds and their metabolite can provide some useful information on the source of OCPs. HCHs are used in two formulations: technical HCH and lindane. Technical HCH contains 60-70 % α -HCH, 10-12 % γ -HCH, 6-10 % δ -HCH, 5-12 % β -HCH, while lindane contains > 99 % γ -HCH¹⁹. The original ratios of α -/ γ -HCH and α -/ β -HCH for technical HCH are generally around 5-7 and 5-14, respectively. Technical HCH has been banned in 1983 while lindane is still being consumed in China, so ratio of α -/ γ -HCH could be used to monitor the source (technical HCH or lindane) and ratio of α -/ β -HCH could be used to estimate the history of the usage of technical HCH (fresh or historical). The high α -/ γ -HCH ratio in soils suggests the historical usage of technical HCH, while a low ratio indicates recent input of lindane. In our study, the ratio of α -/ γ -HCH in farmland soil of Xi'an varied from 0.6-6.3 (Table-3) with an average value of 1.5, while the ratio of α -/ β -HCH ranged from 0.2-0.8 with a mean value of 0.4. These suggested that there has not been fresh input of technical HCH and lindane in Xi'an area.

Technical DDT generally contains 77.1 % *p,p'*-DDT, 4 % *p,p'*-DDE and 14.9 % *o,p'*-DDT²⁰. The ratio of *p,p'*-DDT/*p,p'*-DDE can be used to estimate the age of DDT since DDT can be converted to DDE under aerobic condition²¹. A small ratio of *p,p'*-DDT/*p,p'*-DDE (< 1) indicates historical usage, while a value much greater than 1 suggests fresh inputs²². In this study, as shown in Table-3, the ratio of *p,p'*-DDT/*p,p'*-DDE for the 25 soil samples ranged from 0-2.0 with a mean value of 0.7, which is higher than Beijing^{8,9} but lower than Harbin¹¹ and Guangzhou¹⁰. The relatively lower value of *p,p'*-DDT/*p,p'*-DDE indicates that there is no recent introduction of technical DDT in the study area.

The ratio of α -chlordane/ γ -chlordane in technical chlordane is 0.77²³. According to previous study, γ -chlordane is easier to degrade, so a ratio of α -Chlordane/ γ -chlordane > 1 can be employed as an indicator of historical usage of technical chlordane. In this study, most of the soil concentrations of γ -chlordane are higher than those of α -chlordane. As shown in Table-3, the ratio of α -chlordane/ γ -chlordane for the 25 soil samples ranged from 0.6-2.4 with a mean value of 1.3. These suggested

TABLE-2
COMPARISON OF MEAN CONCENTRATION FOR DDTs AND HCHS
IN SOILS OF XI'AN WITH OTHER REGIONS IN CHINA (UNIT: ng g⁻¹)

Region	Survey year	Land use	DDTs	HCHs	<i>p,p'</i> -DDT/ <i>p,p'</i> -DDE	α -HCH/ γ -HCH	α -HCH/ β -HCH	References
Xi'an	2012	Agriculture	12.80	3.56	0.7	1.5	0.4	This study
Shanghai	2007	Agriculture	21.4	2.4	-	2.8	-	3
Beijing	2007	Irrigated soils	31.3	1.1	-	-	-	12
Harbin	2006	Urban and suburban	5.4	7.1	2.5	2.7	0.1	11
Beijing	2003	Urban and suburban	38.2	5.8	0.4	0.5	0.2	8
Beijing	2003	Agriculture	77.2	1.5	0.4	1.4	0.7	9
Haining	-	Agriculture	83.0	0.7	-	-	-	6
Guangzhou	2004	Agriculture	64.6	6.2	0.8	1.7	-	10
Hongkong	-	Rural and Urban	0.52	6.2	-	6.0	-	18

TABLE-3
RATIOS OF OCPs FOR SOURCE
IDENTIFICATION IN FARMLAND SOIL OF XI'AN

	p,p'-DDT/ p,p'-DDE	α -HCH/ γ - HCH	α -HCH/ β - HCH	α -Chlordane/ γ - Chlordane
S1	0.6	1.6	0.3	2.4
S2	0.5	1.3	0.4	0.8
S3	0.7	1.6	–	1.4
S4	1.0	1.7	0.4	0.8
S5	1.1	1.6	0.3	1.0
S6	1.4	–	–	1.8
S7	0.0	–	–	1.6
S8	0.0	6.3	0.8	0.6
S9	0.0	1.8	0.6	1.2
S10	1.1	0.8	0.3	1.9
S11	0.0	1.1	0.4	0.7
S12	0.0	1.5	0.3	1.3
S13	2.0	0.8	0.5	1.3
S14	0.5	0.6	0.2	2.3
S15	1.3	2.0	0.5	1.2
S16	0.4	0.6	0.2	1.3
S17	1.5	0.7	0.2	1.4
S18	0.9	1.2	–	2.0
S19	1.7	1.2	–	0.9
S20	0.7	1.7	–	0.9
S21	0.3	1.0	0.2	1.4
S22	0.8	0.8	–	1.1
S23	1.0	0.8	0.4	1.1
S24	0.4	3.1	0.7	1.1
S25	0.3	–	–	0.8

that chlordane in farmland soil of Xi'an were mainly from historical usage. However, the relatively smaller ratio (0.6) of α -chlordane/ γ -chlordane was found in the soil sample from sample S8, indicating the fresh input of technical chlordane.

Conclusion

Twenty five farmland soil samples from Xi'an in the Loess Plateau, China, have been analyzed for 20 OCPs. Our results showed that residues of some OCPs still existed, although the use of most OCPs was forbidden in China from 1982. The mean concentrations of DDTs and HCHs are 12.8 and 3.56 ng g⁻¹, respectively, which was in a medium contamination level in China. The residues of OCPs in most of the soil samples are historical usage, but there is still fresh input of technical chlordane at some site. Basing on the national environmental quality standards for soils of China (GB15618-1995), the

concentrations of HCHs and DDTs in all the soil samples were much lower than the First Grade (50 ng g⁻¹) and were classified as low OCPs pollution.

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