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ORIGINAL PAPER

Distribution, sources and potential risk of HCH and DDT in soils from a typical alluvial plain of the Yangtze River Delta region, China

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Abstract Spatial distribution, sources and potential health risks of organochlorine pesticides (OCPs), including hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), in surface soils ($n = 544$) collected from a typical alluvial plain of the Yangtze River Delta region, China, were elucidated. Concentrations of ΣHCH and ΣDDT in soils ranged from less than the limit of detection (<LOD) to 99.0 ng g^{-1}, dry weight (dw) (mean 3.23 ng g^{-1} dw) and <LOD to 600 ng g^{-1} dw (mean 88.8 ng g^{-1} dw), respectively. Historical applications of HCH and DDT were the major sources of the residue in soils. HCH was mainly distributed in Anthrosols in the southern part of the watershed, while DDT was mainly distributed in Cambosols in the northern part. The 95 % cumulative probability incremental lifetime cancer risks (ILCRs) of different age groups such as children, youths, and adults all exceeded the acceptable risk level of 10^{-6} recommended by USEPA for carcinogenic chemicals. The spatial distributions of ∑ILCRs were consistent with concentrations of OCPs in soils, while they were slight different for the different age groups. Adult females had the greatest risk of OCPs in soils, followed by children, while youths had the least risk. The ingestion of OCPs in soils was the more important route of exposure compared with dermal and inhalation exposures. The concentration of OCPs in soils, the particulate emission factor, the fraction of dermal exposure ratio, and the soil ingestion rate were the major contributing variables to total ILCRs according to sensitivity analyses.

Keywords Organochlorine pesticides · Principal component analysis · Kriging · Incremental lifetime cancer risks (ILCRs) · Health risk assessment

Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) are endocrine-disrupting chemicals often associated with adverse health effects in non-target organisms, suggesting that they have potential toxic effects on the human hormonal systems (Lemaire et al. 2004; USEPA 2009). Several OCPs such as α-HCH, β-HCH, γ-HCH (lindane), and DDT were listed as priority persistent organic pollutants (POPs) by the United Nations Environment Program in the Stockholm Convention of POPs. However, although production of

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both technical HCH and DDT was officially banned in China in 1983, they are still detectable at considerable levels in some soils in China (Feng et al. 2003; Hu et al. 2010a; Li et al. 2006; Tao et al. 2008; Wang et al. 2009). Soil is often a significant sink and potential source of contaminants that can result in exposure of humans through ingestion, inhalation, and dermal absorption, thus affecting people's health (Oliver 1997; Shifrin et al. 1996). Even though the agricultural applications of these OCPs were terminated more than three decades ago, their residues remain in the soils and continue to represent a significant public health concern (Miglioranza et al. 2003; Tao et al. 2008).

The Yangtze River Delta (YRD) region lies in the east of China, holding the highest population density and having the fastest economic development of provinces in China. Intensive farming has been conducted there because to the rising demand for agricultural products from urban areas (Hu et al. 2011; Huang et al. 2011), and thus large amounts of OCPs were intensively used historically as insecticides on the croplands to increase agricultural production (Li et al. 1999, 2008; Yang et al. 2008; Zhang et al. 2009). Several studies of OCPs in different environmental media have been conducted in the YRD region (Feng et al. 2003; Li et al. 2008; Tang et al. 2007, 2012; Yang et al. 2005; Zhang et al. 2009), though few studies have systematically reported the spatial distribution of OCPs, and thus their health risk, in soils in the alluvial plain. Therefore, the contamination status of HCH and DDT, their sources, spatial distribution, and potential health risks in soils collected from a typical alluvial plain of the YRD region, China, were comprehensively investigated in this study.

The specific objectives of the present paper were to: (1) determine spatial distribution and sources of HCH and DDT in soils in the typical alluvial plain of the YRD region, China; (2) evaluate incremental lifetime cancer risks (ILCRs) to the inhabitants due to exposure to HCH and DDT in soils; and (3) identify the major influential variables in the ILCRs of OCPs from different exposure routes.

Materials and methods

Study area and sample collection

This study focused on a typical flat alluvial plain in the YRD region of China (31°43′–32°01′N, 120°22′–120°49′E), Zhangjiagang City, which covers a total terrestrial area of 799 km^2 with an arable land area of 409 km^2. The main soil types in the study area can be divided into two soil orders, Anthrosols (Paddy soils) and Cambosols (Fluvo-aquic soils) (CRGCST 2001; Huang et al. 2011). From the 1960s to the 1980s, large amounts of pesticides, including HCH and DDT, were applied in the croplands of Zhangjiagang City, especially for cotton on the Cambosols and rice on Anthrosols. A total of 544 topsoil samples were collected in 2004 throughout the watershed based on soil types, land uses, and spatial homogeneity (Fig. 1). The sampling design has been previously described in detail (Hu et al. 2011). Fresh soil samples (about 1 kg) were transported to the laboratory in polyethylene ziplock bags, lyophilized, sieved through a 2-mm mesh, and then stored at 4 °C in pre-cleaned glass jars until analysis.

Extraction, cleanup and quantification

The analytical method is similar to that described previously (Hu et al. 2011). Each soil sample [5.0 g dry weight (dw)] was mixed with 1 g anhydrous sodium sulfate (analytical grade). One milliliter of 2,4,5,6-tetrachloro-*m*-xylene at the concentration of 0.08 μg/mL was added. The mixture was extracted twice with 35 mL of hexane/dichloromethane (1:1, v/v) by ultrasonication for 60 min and then centrifuged. Extracts were concentrated to about 2 mL by rotary evaporation, and further purified with solid phase extraction (SPE, 6 mL; Supelco, Bellefonte, PA, USA) cartridges loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. The elution was subsequently carried out using 20 mL of hexane/dichloromethane (7:3, v/v). The eluant was concentrated to a final volume of 1 mL for gas chromatograph (GC) analysis. Reagent blanks were also analyzed simultaneously with the experimental samples. The purified eluant was analyzed using GC-μECD (Agilent Technologies, Wilmington, DE, USA) under splitless injection mode with ultrapure nitrogen as the carrier gas and the make-up gas. The injector and detector temperatures were 220 and 300 °C, respectively. The oven temperature was initially set at 100 °C with a 2-min hold, ramped at 10 °C/min to 160 °C with a 2-min hold, 4 °C/min to 230 °C with a 5-min hold, and then 10 °C/min to 270 °C with a 2-min hold. Organochlorine pesticides were identified by retention time

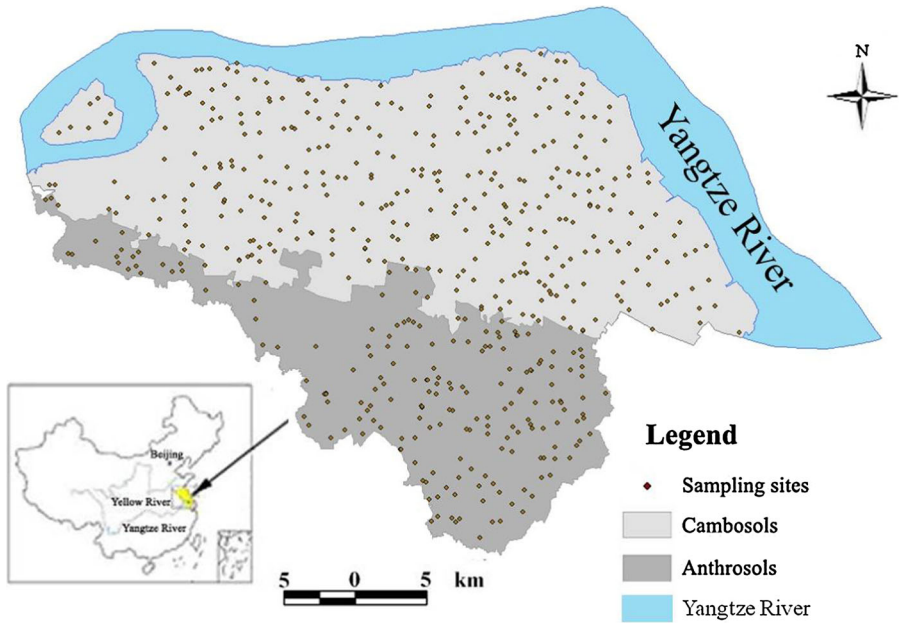

Fig. 1 Study area and sampling sites of the typical alluvial plain of the YRD region, China

matched to standards and were quantified using peak area integration.

For quality assurance and quality control, procedural blanks and matrixes spiked with the standard solution were analyzed. A mixture of a standard solution containing α-, β-, γ-, δ- HCH isomers, *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, and *p,p′*-DDT at 1 mg/g per compound was obtained from the National Research Center for Certified Reference Materials of China. None of the target compounds was detected in the procedural blanks. All solvents used were distilled in glass (PR grade) and were checked for interferences or contamination prior to use. The recoveries of OCPs spiked to soil ranged from 73.1 to 109 % ($n = 3$). Extraction efficiency, as indicated by recovery of the surrogate standards (2,4,5,6-tetrachloro-*m*-xylene), was 85 ± 10 %. The limits of detection (LOD) were described as three times the signal-to-noise ratio (S/N). The detection limit ranged from 0.05 to 0.40 ng g^{-1} dw. Gas chromatograph analysis was repeated twice for each replicate sample and the relative standard deviation (RSD) of replicate analyses were between 5 and 18 %.

Health risk assessment

Incremental lifetime cancer risks (ILCRs) of OCPs in soils were evaluated following USEPA standard models (Peng et al. 2011; USEPA 1991). In order to reduce computation, it was assumed that an estimate of the increased cancer incidence to a receptor from a single chemical exposure in the whole area was via the three exposure routes, e.g., inhalation, dermal contact, and direct ingestion exposure as follows (Eqs. 1, 2, 3)

$$\mathrm{ILCRs_{Inhalation}} = \frac{C_s \times \left(\mathrm{CSF_{Inhalation}} \times \sqrt[3]{(\mathrm{BW}/70)}\right) \times \mathrm{IR_{air}} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT} \times \mathrm{PEF}} \quad (1)$$

$$\mathrm{ILCRs_{Dermal}} = \frac{C_s \times \left(\mathrm{CSF_{Dermal}} \times \sqrt[3]{(\mathrm{BW}/70)}\right) \times \mathrm{SA} \times \mathrm{FE} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT} \times 10^6} \quad (2)$$

$$\mathrm{ILCRs_{Ingestion}} = \frac{C_s \times \left(\mathrm{CSF_{Ingestion}} \times \sqrt[3]{(\mathrm{BW}/70)}\right) \times \mathrm{IR_{soil}} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT} \times 10^6} \quad (3)$$

where C_s is the OCPs concentration of soils (ng g^{-1}), CSF is the carcinogenic slope factor (mg kg^{-1} $day^{-1})^{-1}$, BW is the body weight (kg), AT is the average life time for carcinogens (days), EF is the exposure frequency (day $year^{-1}$), ED is the exposure duration (years), IR_{air} is the inhalation rate of air (m^3 day^{-1}), IR_{soil} is the ingestion rate of soil (mg day^{-1}), SA is the skin surface area for soil contact (cm^2 day^{-1}), FE is the fraction of dermal exposure ratio to soil, AF is the soil adherence factor (mg cm^{-2}), ABS is the fraction of applied dose absorbed across skin, and PEF is the particulate emission factor (m^3 kg^{-1}). The body function-related parameters and exposure variables were based on China's Health Statistical Yearbook (CMH 2006) and USEPA Integrated Risk Information System (USEPA 2002, 2008) (Table 1).

The carcinogenic slope factor (CSF), based on the cancer-causing ability of OCPs was used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a potential carcinogen, was obtained from the Integrated Risk Information System (USEPA 2002, 2008), including $CSF_{inhalation}$, CSF_{dermal}, and $CSF_{ingestion}$ of HCH and DDT in different exposure methods (Table 2). The ILCRs values for humans were calculated for all exposures. The risks of cancer for children, youths, and adults were calculated separately. Total risks were the sum of risks associated with each exposure route.

In order to determine the major influential factors in ILCRs of OCPs from different exposure routes, a Monte Carlo simulation was used to calculate the uncertainty of estimated risk. In a Monte Carlo analysis, each of the input parameters is represented by a probability density function that defines both the range of values that the parameter can take on and the likelihood that the parameter has a value in any subinterval of that range (Iman and Helton 1988).

Data analysis

Statistical analysis of data was performed using SPSS 17.0 and Microsoft Excel. Concentrations that were less than the LOD were set to half of LOD for statistical purposes. Spearman correlation analysis was used to explore the relationship between HCH and DDT and soil organic carbon contents. Principal component analysis (PCA) was used to explore the sources of HCH and DDT in soils. The software used for mapping the sampling sites was ArcGIS 9.2 software (ESRI, USA). A geostatistical method such as Kriging has been applied to investigate the spatial variability of continuously varying environmental parameters and to predict values for areas that were not sampled (Oliver 1997). The ordinary Kriging interpolation analysis with spherical model was used to construct the spatial map of HCH and DDT. The data were log-transformed as they were log-normally distributed. Crystal Ball 7.2 software (Decisioneering, Denver, CO, USA) was used to calculate the sensitivity of ILCRs by repeating a random sample 5,000

Table 1 Exposure parameters used in the incremental lifetime cancer risk assessment

Exposure variables	Unit	Children		Youths		Adults	
		Male	Female	Male	Female	Male	Female
Body weight (BW)	kg	17.2	16.5	47.1	44.8	60.2	53.1
Exposure frequency (EF)	day $year^{-1}$	350	350	350	350	350	350
Exposure duration (ED)	years	6	6	14	14	30	30
Inhalation rate (IR_{air})	m^3 day^{-1}	10.9	10.9	17.7	17.7	17.5	17.5
Ingestion rate (IR_{soil})	mg day^{-1}	200	200	100	100	100	100
Skin surface area (SA)	cm^2 day^{-1}	1,800	1,800	5,000	5,000	5,000	5,000
Soil adherence factor (AF)	mg cm^{-2}	0.2	0.2	0.2	0.2	0.07	0.07
Dermal adsorption fraction (ABS)	Dimensionless	0.1	0.1	0.1	0.1	0.1	0.1
Dermal exposure ratio (FE)	Dimensionless	0.61	0.61	0.61	0.61	0.61	0.61
Average life time (AT)	days	25,550	25,550	25,550	25,550	25,550	25,550
Particulate emission factor (PEF)	m^3 mg^{-1}	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9

Table 2 The carcinogenic slope factor (mg kg^{-1} day^{-1}) of OCPs in different exposure routes

OCPs	$CSF_{inhalation}$	CSF_{dermal}	$CSF_{ingestion}$
α-HCH	6.3	4.49	6.3
β-HCH	1.86	1.98	1.8
γ-HCH	1.8	1.34	1.3
δ-HCH	1.8	NA	1.8
p,p′-DDD	NA	0.343	0.24
p,p′-DDE	NA	0.486	0.34
p,p′-DDT	0.34	0.486	0.34

NA not available

times, which has been deemed sufficient to avoid unacceptable variance in different realizations.

Results and discussion

Concentrations of HCH and DDT in soils

The concentrations of HCH and DDT in soils are presented in Table 3. HCH isomers were detected in a small part of samples (6–21 %), and total concentrations of HCH varied from less than the limits of detection (LOD) to 99.0 ng g^{-1} dw (with a mean value of 3.23 ng g^{-1} dw), while DDT metabolites were detected above the LOD in the vast majority of the soil samples (54–96 %), and the total concentrations varied from LOD to 600 ng g^{-1} dw (with a mean value of 88.8 ng g^{-1} dw). The high standard deviations of HCH and DDT concentrations indicated intense spatial heterogeneity of HCH and DDT in the study area. This type of patchy distribution is often observed for concentrations of organic residues in soils and leads to non-normal frequency distributions (Hu et al. 2010b). On the whole, the concentrations of ΣDDT in soils were much greater than those of ΣHCH. This result was consistent with the previous measurements of concentrations of HCH and DDT in the soils from the YRD region (Zhang et al. 2009) and Nanjing, China (An et al. 2005), the soils of the Haihe Plain, China (Tao et al. 2008), the soils in the vicinity of watersheds of Beijing Reservoirs, China (Hu et al. 2010a), and the agricultural soils of central Germany (Manz et al. 2001). HCH is more water soluble and has a greater vapor pressure, biodegradability, and lesser Kow and Kd values, relative to DDT, which may account for the relatively small amounts of HCH residues in soils (Hu et al. 2010c).

Spatial distribution of HCH and DDT in soils

Understanding the occurrence and spatial variability of toxic substances can further illuminate the role of anthropogenic activities in releasing these compounds to the environment, and provide information to assist in devising effective strategies to mitigate potential health effects (Marvin et al. 2004). The distribution patterns of ∑HCH and ∑DDT were significantly different in soils from the typical alluvial plain of the YRD region (Fig. 2). The concentration of ∑HCH in

Table 3 Concentrations (ng g^{-1} dw) of HCH and DDT in soils from the typical alluvial plain of the YRD region of China

OCPs	Mean	SD	Minimum	Maximum	Median	95-percentile	DR[b] (%)
α-HCH	0.107	0.489	<LOD	5.31	0.01	0.409	6.25
β-HCH	0.323	1.07	<LOD	12.8	0.01	1.74	16.9
γ-HCH	0.788	2.43	<LOD	18.0	0.00	4.09	21.1
δ-HCH	2.01	8.16	<LOD	91.5	0.00	11.9	16.0
ΣHCH[a]	3.23	10.3	<LOD	99.0	0.02	18.0	21.7
p,p′-DDE	49.0	61.7	<LOD	344	23.3	198	95.8
p,p′-DDD	9.85	11.6	<LOD	86.8	7.02	27.4	93.9
o,p′-DDT	4.93	8.38	<LOD	61.2	0.75	25.5	53.9
p,p′-DDT	25.0	37.2	<LOD	385	15.0	69.0	88.2
ΣDDT[a]	88.8	119	<LOD	600	46.0	320	96.1

SD standard deviation

[a] ΣHCH = α-HCH + β-HCH + γ-HCH + δ-HCH, ΣDDT = *p,p′*-DDE + *p,p′*-DDD + *o,p′*-DDT + *p,p′*-DDT

[b] *DR (%)* detectable ratio (detectable ratio = the number above the LOD for each OCPs/544 × 100 %)

soils was significantly greater in the southern part of the watershed (Fig. 2a). Anthrosols are the dominant soils on the plains of the southern part of the watershed, developed from lacustrine deposits on alluvium, with a loamy clay texture (SSOZC 1984). In these areas, the dominant planting system had always been the rotation of rice and wheat. According to our investigation, considerable amounts of pesticides were used in these areas in the past. Restriction on the use of HCH has brought a general decrease in ∑HCH concentrations in soils, but the rate of decrease has been slow. As a result, concentrations of HCH in these areas were greater than those in other areas. Areas with higher DDT concentrations were mainly located in the northern part of the watershed along the Yangtze River (Fig. 2b), where Cambosols are the dominant soils developed from neo-alluvium parent materials with light-medium loamy texture (SSOZC 1984). In the Cambosols before the 1980s, the rotation of cotton as summer crop and wheat as winter crop was dominant,

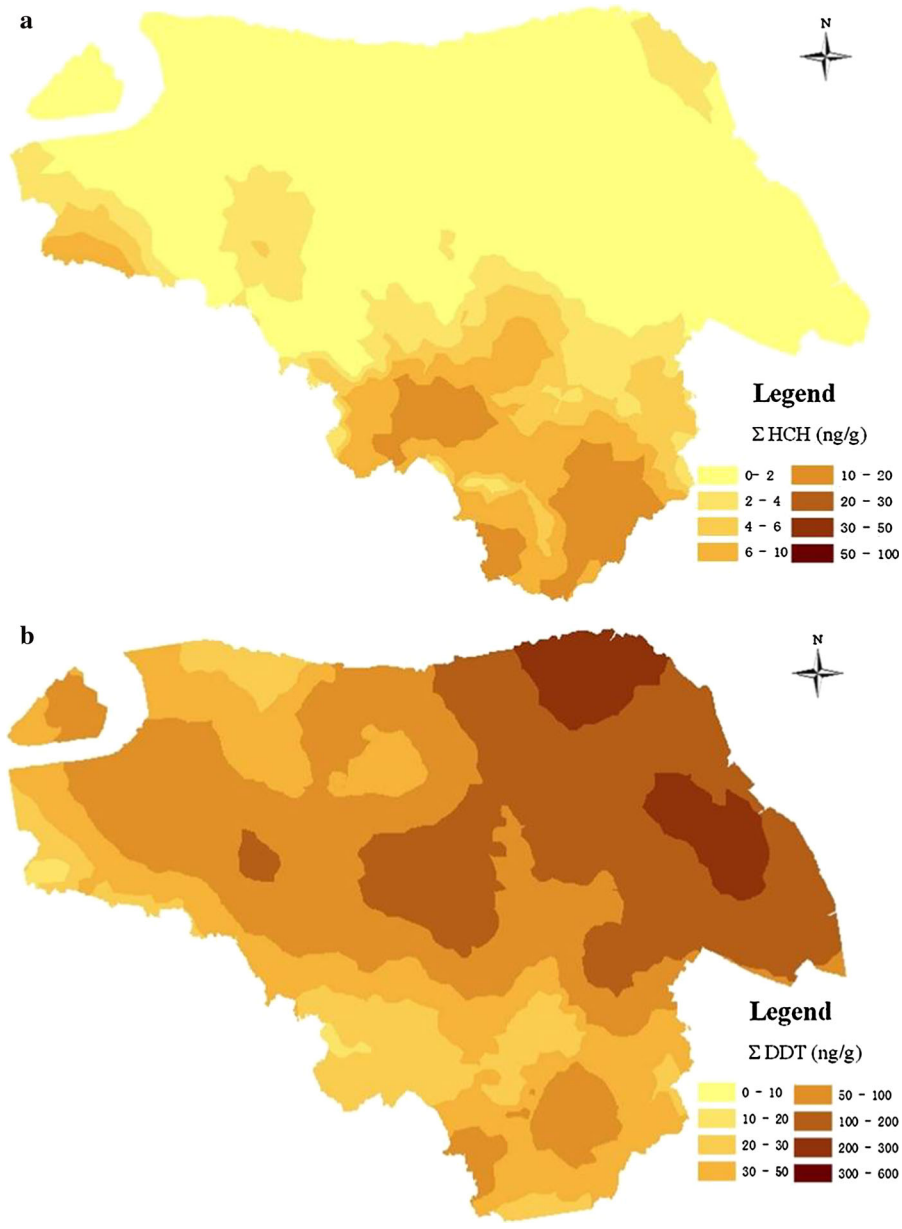

Fig. 2 Spatial distribution patterns of ∑HCH (**a**) and ∑DDT (**b**) in soils

although, after the 1980s, most of the cotton has been increasingly substituted with rice. Historically heavy applications of DDT pesticides for cottons were identified in these areas. Overall, the observed variation of HCH and DDT in soils suggested that the occurrence and distribution of the ∑HCH and ∑DDT were mainly dependent on historical application. From 1950 to 1983, an estimated more than 4 million tons of ∑HCH and total of 0.46 million tons of ∑DDT were produced in China with most of the production applied in agriculture (Tao et al. 2008).

To further explore the factors affecting HCH and DDT variation in soils in the study area, soil organic carbon contents in Anthrosols and Cambosols were compared. Organic carbon contents in Anthrosols (mean 25.3, range 8.58–38.3) were greater than those of Cambosols (mean 19.4, range 5.31–36.8). Significant positive correlations among α-HCH ($p < 0.05$), β-HCH ($p < 0.01$), γ-HCH ($p < 0.01$), δ-HCH ($p < 0.01$), and ∑HCH ($p < 0.01$) with organic carbon contents were found, which suggests sorption of HCH to soil organic carbon. Significant negative correlations among *p,p′*-DDE, *o,p′*-DDT, and ∑DDT with organic carbon contents were found ($p < 0.01$). Greater organic carbon contents in soils can allow a larger microbial biomass and thus can induce the degradation of DDT (Wang et al. 2007). As a result, concentrations of DDT in Anthrosols were lower than those of Cambosols. The results indicated that soil organic carbon was also involved in HCH and DDT retention and distribution in soils.

Source identification using principal component analysis (PCA)

Contribution of individual sources fpr the total HCH and DDT could be attained by principal component analysis (PCA). As a multivariate statistical tool, the PCA approach has been widely used to identify potential or even likely sources of contaminants and their degradation behavior (Manz et al. 2001; Skrbic and Durisic-Mladenovic 2007). The results of sorted rotated factor loading scores along with eigenvalues and cumulative variances are listed in Table 4.

For HCH, 77.4 % of total variance was explained by the first two factors (Table 4). The first PC (PC1), accounting for 51.6 % of total variance, had large positive loadings for β-HCH (0.80), γ-HCH (0.82), and δ-HCH (0.74). Since the γ-HCH content of lindane is approximately 99.9 %, PC1 primarily explained the sources of lindane. The second PC (PC2), which explained 25.8 % of total variance, was characterized by absolute loading of α-HCH (0.82) which were statistically significant, while loadings of β-HCH (0.23), γ-HCH (−0.24), and δ-HCH (−0.50) were relatively small. For technical HCH, α-HCH is the main isomer compared with other isomers. Among the HCH isomers, α-HCH is more likely to partition to the air and be transported for long distances (Willett et al. 1998). The major loading of α-HCH showed that PC2 was mostly related to the degradation of "old" technical HCH. When PCA was performed for DDT, two factors were extracted and accounted for 80.7 % of the total variance in the dataset. DDT metabolites were all included in factor 1 (PC1), which explained 56.7 % of the total variance. Most loadings of *p,p′*-DDE (0.79), *p,p′*-DDD (0.83), and *p,p′*-DDT (0.82) and more than half the loading of *o,p′*-DDT (0.52) were involved. For technical DDT, *p,p′*-DDT is the major transformation product compared with other products. According to the composition and degradation rules of technical DDT, PC1 was mostly related to the degradation of technical DDT. The second factor (PC2), which accounted for 24.0 %, was dominated by *o,p′*-DDT (0.79), with little positive loading to *p,p′*-DDE (0.26) and little negative loading related to *p,p′*-DDD (−0.40) and *p,p′*-DDT (−0.34). Since the *o,p′*-DDT was considered to be the major impurity

Table 4 Principal component analysis (PCA) for the source apportionment of selected OCPs

Compounds	Component	
	Factor 1	Factor 2
α-HCH	0.46	**0.82**
β-HCH	**0.80**	0.23
γ-HCH	**0.82**	−0.24
δ-HCH	**0.74**	−0.50
Eigenvalue	2.07	1.03
Cumulative percentage (%)	51.6	77.4
p,p′-DDE	**0.79**	0.26
p,p′-DDD	**0.83**	−0.40
o,p′-DDT	0.52	**0.79**
p,p′-DDT	**0.82**	−0.34
Eigenvalue	2.27	0.96
Cumulative percentage (%)	56.7	80.7

Significant values were shown in bold

compound in dicofol, factor 2 can primarily explain the sources of dicofol. In general, because the use of HCH and DDT pesticides in China was banned in the early 1980s, the presence of their residues in soils was predominantly from previous usage (Hu et al. 2011). The pattern of HCH was a mixture of historical technical HCH and lindane sources, while the DDT pollution was consistent with historical releases of technical DDT and agricultural use of dicofol. The persistent nature of these types of compounds together with continued illegal use of banned OCPs raises the potential for continued long-term chronic exposure with effects on human health.

Health risk assessment of HCH and DDT in soils

To set the current concentrations of OCPs in surface soils into a health risk perspective, incremental life cancer risks (ILCRs) were employed to explore the potential risks to humans. The ILCR accounts for integrated lifetime risks of being exposed to soil-borne OCPs through the combination of inhalation, dermal contacts, and direct ingestion. The 95-percentile risk distribution is often considered to be the starting point for risk management (Yang et al. 2009). In regulatory terms, an ILCR of 10^{-6} or less denotes virtual safety and an ILCR of greater than 10^{-4} denotes a potentially large risk (Liao and Chiang 2006; USEPA 1992, 1996).

The ILCRs of HCH, DDT, and the total OCPs' intake from soil over all exposure routes for three age groups were calculated and are shown in Table 5. Among the OCPs, the proportions contributed by HCH and DDT to the $\sum$ILCRs were approximately 15 and 85 %, respectively. Although the cancer slope factors of HCH were greater than those of DDT (Table 2), the residue levels of HCH in soils were significantly lower than those of DDT, leaded to the lower contribution by HCH to the $\sum$ILCRs. The 95 % cumulative probability ILCRs for adults exposed to the total OCPs concentration of soils were 8.46×10^{-5} for males and 9.20×10^{-5} for females, respectively, which were the greatest risks among three age groups. The risks for youths were less than for children or adults. The average 95 percentile of estimated ILCRs for children, youths, and adults were all less than 10^{-4}, but these values exceeded the generally acceptable risk level recommended by USEPA for carcinogenic chemicals

Table 5 ILCRs of three exposure approaches of HCH and DDT for different age groups

	Children		Youths		Adults	
	Male	Female	Male	Female	Male	Female
HCH						
Mean	3.67×10^{-6}	3.77×10^{-6}	1.38×10^{-6}	1.42×10^{-6}	4.13×10^{-6}	4.49×10^{-6}
Minimum	4.74×10^{-8}	4.88×10^{-8}	2.35×10^{-8}	2.43×10^{-8}	5.53×10^{-8}	6.01×10^{-8}
Maximum	1.06×10^{-4}	1.09×10^{-4}	2.97×10^{-5}	3.07×10^{-5}	1.16×10^{-4}	1.26×10^{-4}
Median	4.74×10^{-8}	4.88×10^{-8}	2.35×10^{-8}	2.43×10^{-8}	5.53×10^{-8}	6.01×10^{-8}
95 percentile	2.50×10^{-5}	2.57×10^{-5}	8.28×10^{-6}	8.56×10^{-6}	2.8×10^{-5}	3.05×10^{-5}
DDT						
Mean	1.91×10^{-5}	1.96×10^{-5}	1.84×10^{-5}	1.90×10^{-5}	2.33×10^{-5}	2.54×10^{-5}
Minimum	2.77×10^{-9}	2.85×10^{-9}	2.67×10^{-9}	2.76×10^{-9}	3.39×10^{-9}	3.68×10^{-9}
Maximum	1.37×10^{-4}	1.40×10^{-4}	1.32×10^{-4}	0.000136	1.67×10^{-4}	1.82×10^{-4}
Median	1.09×10^{-5}	1.12×10^{-5}	1.05×10^{-5}	1.08×10^{-5}	1.33×10^{-5}	1.44×10^{-5}
95 percentile	6.53×10^{-5}	6.71×10^{-5}	6.30×10^{-5}	6.51×10^{-5}	7.99×10^{-5}	8.69×10^{-5}
Total OCPs						
Mean	2.27×10^{-5}	2.34×10^{-5}	1.98×10^{-5}	2.04×10^{-5}	2.75×10^{-5}	2.98×10^{-5}
Minimum	5.02×10^{-8}	5.16×10^{-8}	2.62×10^{-8}	2.71×10^{-8}	5.87×10^{-8}	6.38×10^{-8}
Maximum	1.80×10^{-4}	1.85×10^{-4}	1.45×10^{-4}	1.50×10^{-4}	2.15×10^{-4}	2.34×10^{-4}
Median	1.44×10^{-5}	1.48×10^{-5}	1.19×10^{-5}	1.23×10^{-5}	1.75×10^{-5}	1.90×10^{-5}
95 percentile	6.99×10^{-5}	7.19×10^{-5}	6.45×10^{-5}	6.67×10^{-5}	8.46×10^{-5}	9.20×10^{-5}

of 10^{-6}. As HCH and DDT were pervasive in soils of the study areas, the cancer risk due to exposures to HCH and DDT was deemed to be exceptional. The cancer risk for women exposed to OCPs was slightly greater than that for men; however, the difference was not significant. This was mainly due to the differences in body weight between men and women.

Risk assessment strategies are often aimed at population subgroups. It is common practice to identify vulnerable populations, such as young

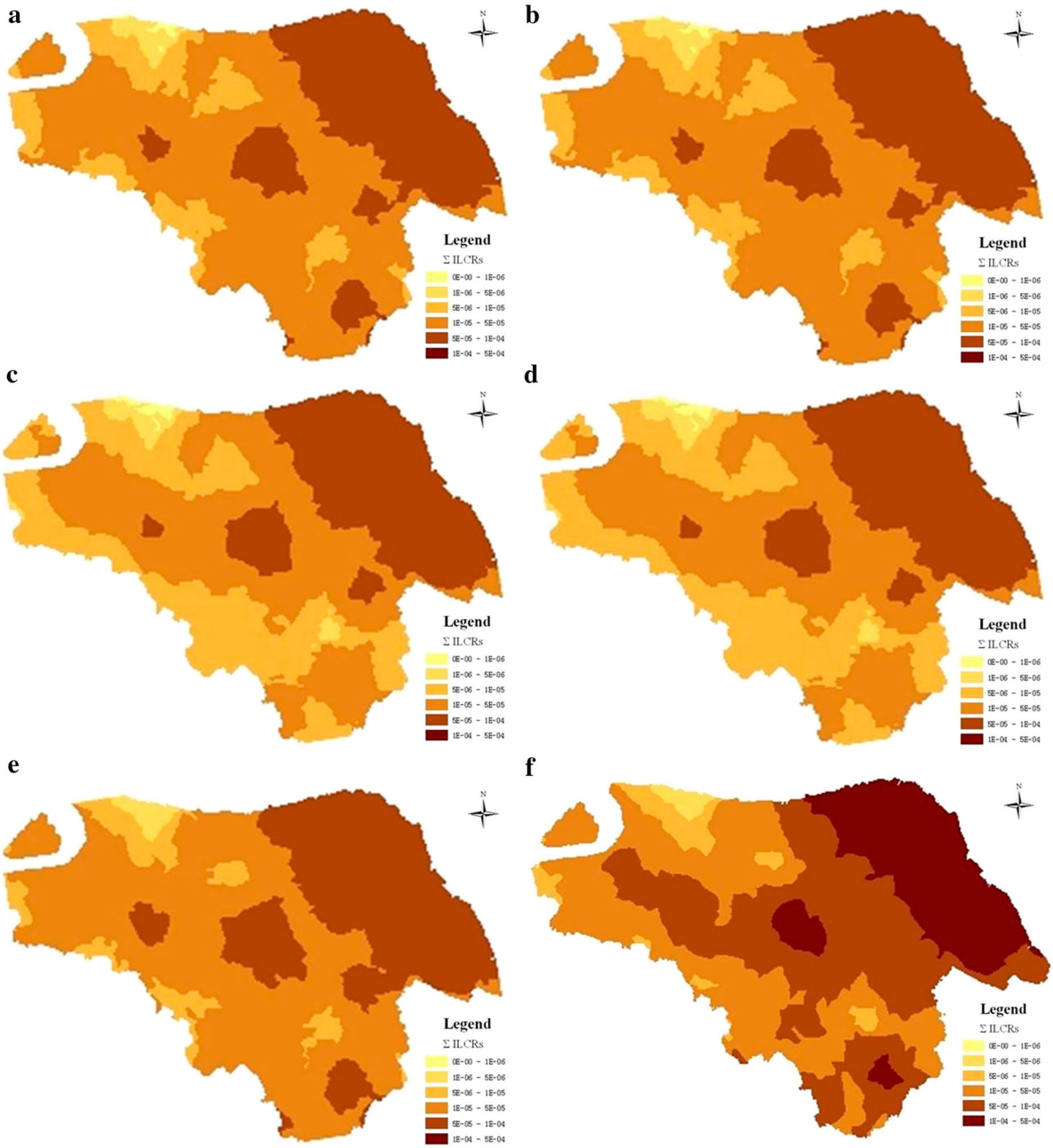

Fig. 3 Spatial distribution patterns of ΣILCRs for child male (**a**), child female (**b**), youth male (**c**), youth female (**d**), adult male (**e**), and adult female (**f**)

children or the elderly, and assess potential risks to the health of these population subgroups (Hough et al. 2004). Thus, the ∑ILCRs of different age groups were further analyzed to determine the spatial distribution of ILCRs (Fig. 3). The first stage was classified as a risk for ∑ILCRs that was less than 10^{-6}, which is presented in the figure as the lightest color. Except for the lightest color, the potential values for ∑ILCRs were greater than 10^{-6}. The darker the shading in the figure, the greater the potential cancer risk. The spatial distribution of ∑ILCRs in soils in the study region was closely associated with the HCH and DDT residue status in soils. The ILCRs of children, youths, and adults in areas of high soil OCPs concentration were in the same order of magnitude as those under average exposures. The spatial pattern of ∑ILCRs varied only slightly among different age groups. Adult females had the greatest risk among the three age groups (Fig. 3f), followed by children (Fig. 3a, b), and youths (Fig. 3c, d). Therefore, if the risk of highly exposed subpopulations of adult females to the ILCRs is acceptable then most of the population is protected. As for ∑ILCRs of adult females, only about 3.31 % of soils in the whole area had a risk that was less than 10^{-6}. Approximately 94.12 % of the area had a risk level of 10^{-6} to 10^{-4}, while in approximately 2.57 % of the area the risk level exceeded 10^{-4}, which was located in the area with higher HCH and DDT residues in soils. These results suggest that the potential cancer risks to local residents due to exposure to OCPs in soils in some contaminated sites should be paid more attention by the government and by decision makers.

The 95 % cumulative probability ILCRs in different exposure routes and different types of people are shown in Fig. 4. The ILCRs in different exposure routes decreased in the following order: direct ingestion > dermal contact > inhalation. The ILCRs caused by inhalation of soil particles were small among the three exposure routes, which were approximately 10^{-10} to 10^{-9}, and so less than 10^{-6}. This indicated that the cancer risk caused by the inhalation of soil particles was negligible. Because of the longer exposure time and greater air intake amount, the ILCRs caused by inhalation for adults were the greatest and the ILCRs for children were the smallest. Based on exposure through dermal contact, the values of ILCRs among the three age groups exceeded 10^{-6}. Among them, the ILCRs values for youths were the greatest, followed by those for adults, while the ILCRs for children were the least. This was due to the smaller skin surface areas in children, which led to smaller ILCRs caused by skin contacts. Although youths have smaller skin surface areas compared to adults, their dermal adherence factor (AF) is larger (0.2 for youths,

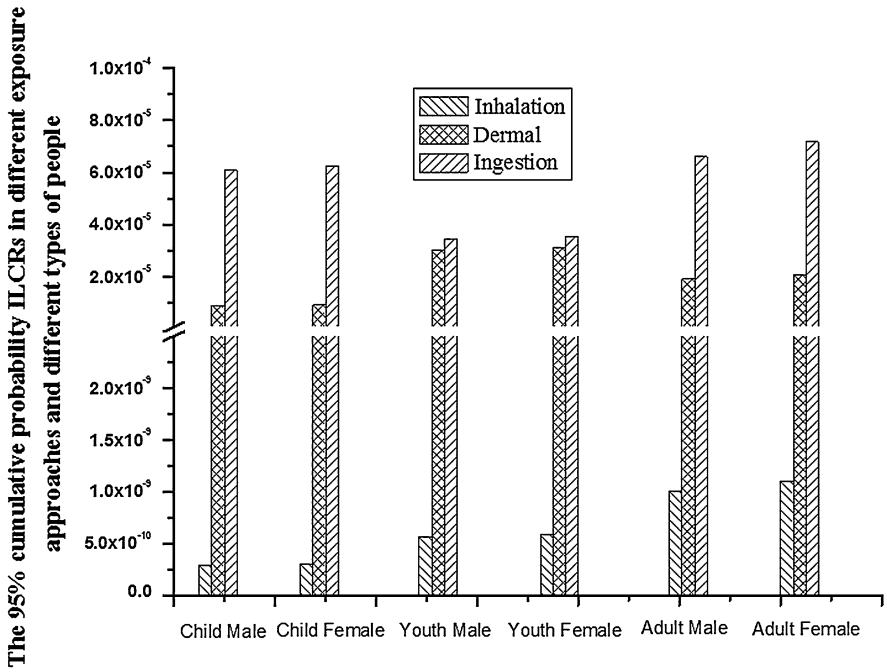

Fig. 4 The 95 % cumulative probability ILCRs of OCPs for different exposure routes and different types of people

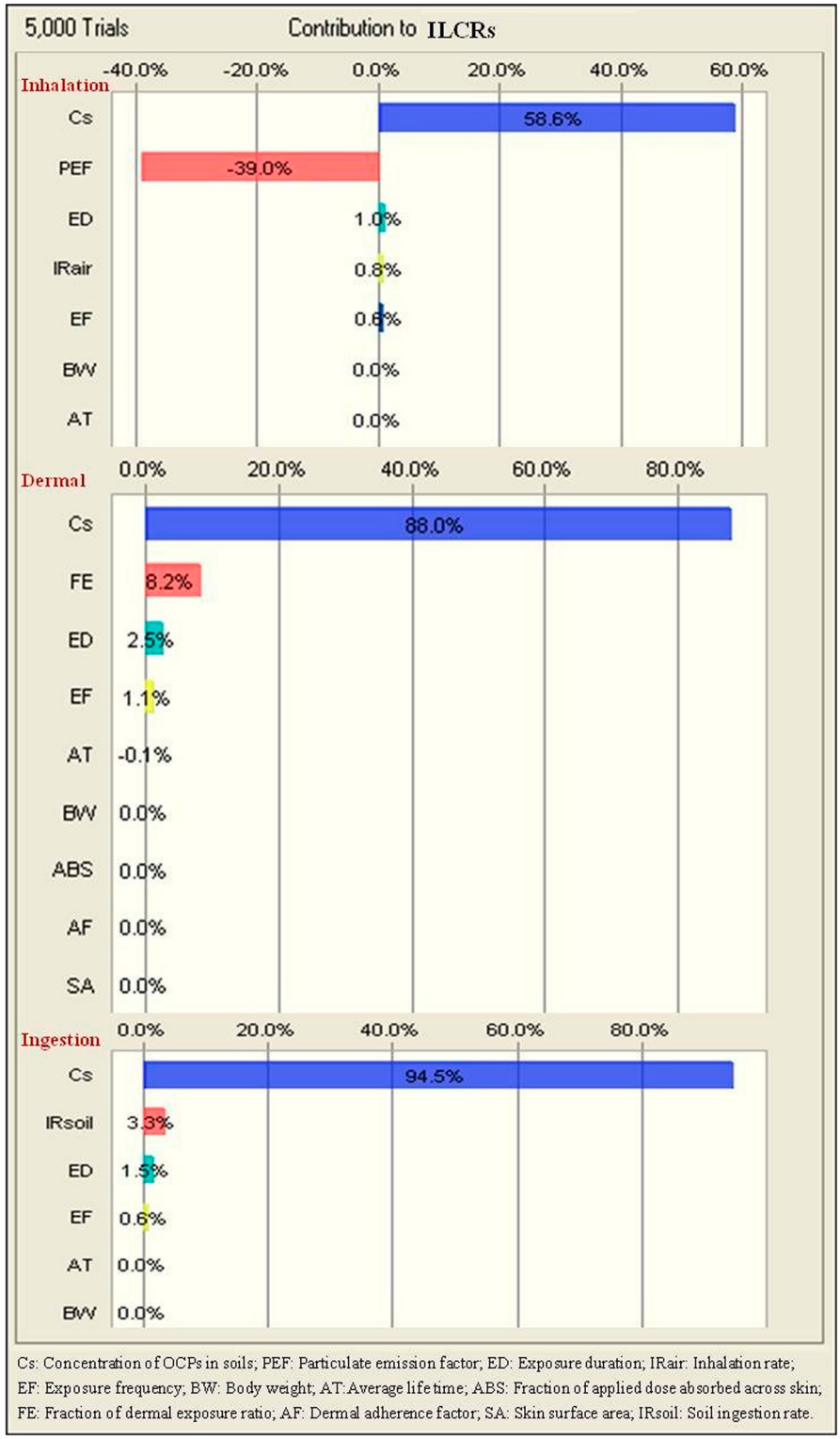

Fig. 5 The contribution of different variables of three exposure approaches for total ILCRs

and only 0.07 for adults), and the impacts of these factors resulted in the ILCRs of youths becoming the greatest, and for children the smallest. The 95 % probability of ILCRs through soil ingestion by children and adults were similar and are both greater than those by youths (Fig. 4). Children are naturally active, and the soil ingestion can be significantly greater than that by youths and adults, which leads to greater cancer risk caused by soil ingestion. As for adults, although the ingestion rate of soil (IR_{soil}) is relatively small, the longer exposure time can result in a cancer risk in adults that is similar to the risk caused by soil ingestion in children. Due to a lesser rate of ingestion of soil and shorter exposure time, the ILCRs for youths were smaller. In general, the direct ingestion and dermal contact exposure to soil OCPs played an important role in the health risk for children and adults, which should be taken into consideration by some of the decision makers and researchers.

Sensitivity analysis

In order to determine the major influential factors in the ILCRs of OCPs from different exposure routes, we conducted sensitivity analyses using Crystal Ball 7.2 software. Sensitivity analysis is used to rank the input variables on the basis of their contribution to variance in the output, because information is a driving factor in the overall uncertainty of risk estimates for populations (Chen and Ma 2006). The results of sensitivity analyses of ILCRs in the three exposure routes are listed in Fig. 5. For inhalation exposure, concentrations of OCPs in soils (C_s) and the particulate emission factor (PEF) were the most sensitive parameters. The contribution of C_s to the ILCRs was exceeded by 58.6 %, while the contribution of PEF shows a negative correlation, approximately accounting for −39.0 %. The findings suggest that C_s and PEF played significant roles in the human inhalation exposure risk of OCPs in soils. Exposure duration (ED) and inhalation rate (IRair) also played important roles in ILCRs.The contribution of body weight (BW) and average life time (AT) to ILCRs were the smallest, close to 0 %. As for the dermal exposure, the major contribution variables were C_s, the fraction of the dermal exposure ratio to soil (FE), which contributed 88.0 and 8.2 %, respectively. Exposure frequency (EF) and ED also played important roles in ILCRs. Concerning the soil ingestion exposure, the most important influential factors were C_s and soil ingestion rate (IRsoil), and the contribution rates were 94.5 and 3.3 %, respectively. The ED, EF, and other parameters were comparatively less sensitive. In general, the sensitivity analyses indicated that C_s, PEF, FE, and IRsoil were the relatively higher sensitive variables in total ILCRs. Because of the persistence of OCPs in soils and their transport through the environmental media, the implication of sensitivity from our results suggested that risk management should be introduced to the OCPs-contaminated sites in order to achieve an acceptable level of risk for the local inhabitants.

Conclusions

The selected OCPs, especially DDT, were pervasive in the soils of the typical alluvial plain of the Yangtze River Delta region, China. Historical agricultural application of HCH and DDT was the major source of their residues according to spatial and PCA analysis. Based on the distribution patterns, the areas of high HCH and DDT concentration and potential health risk soils were identified. The 95 % ILCRs of the total OCPs for children, youths, and adults all exceeded the generally acceptable risk level of 10^{-6}. The spatial pattern of $\sum$ILCRs varied only slightly among different age groups. Females had a slightly greater cancer risk than that of males, and, among the age groups, adult females had the greatest risk. According to sensitivity analysis, the major influential variables in the ILCRs of OCPs from different exposure routes were identified. The concentrations of OCPs in soils (C_s), the particulate emission factor (PEF), the fraction of dermal exposure ratio (FE)s and the soil ingestion rate (IRsoil) were the most sensitive variables in total ILCRs.

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