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Fishpond sediment-borne DDTs and HCHs in the Pearl River Delta: Characteristics, environmental risk and fate following the use of the sediment as plant growth media

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ABSTRACT

Investigation was made to characterize the fishpond sediment-borne DDTs and HCHs in a dyke-pond integrated agriculture–aquaculture system. Microcosm experiment was conducted to track the fate of DDTs and HCHs following the use of the sediment as plant growth media. The ratios of DDT/DDE + DDD, o,p′-DDT/p,p′-DDT and DDD/DDE were over 4, over 2 and nearly 2, respectively. These suggest that fresh DDT inputs from dicofol application are likely and anaerobic decomposition was the major pathway of DDT degradation. The sediments had higher percentage of δ-HCH and lower percentage of γ-HCH, compared to technical HCH. The levels of both DDTs and HCHs were higher in the sediments, as compared to those in the estuarine sediments and fishpond sediments in non-traditional dyke-pond system. The sediment-borne DDTs and HCHs posed an environmental threat to the local ecosystem. Upon its use as plant growth media, the majority of DDTs was retained in the soil while <1/3 of the original soil-borne DDTs were lost; no leaching loss was recorded and plant uptake was negligible. Only <20% of the original soil-borne HCHs were retained in the soil while leaching loss accounted for 1.24%; nearly 79% of the original soil-borne HCHs disappeared as a result of HCHs degradation and possibly volatilization.

1. Introduction

The extensive application of organochlorine pesticides prior to the global restriction on their uses resulted in widespread presence of some synthesized chemicals such as dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) in the environment [1–3]. It has been well established that both DDT and HCH have significantly adverse effects on human health and ecosystems [4–10]. DDT can degrade to produce chlorodiphenyldichloroethylene (DDE) primarily under aerobic conditions and dichlorodiphenyldichloroethane (DDD) predominantly under anaerobic conditions [11,12]. The code DDTs has been widely used to stand for the sum of DDT, DDE and DDD. There are four major isomers of HCH in technical HCH: α-HCH, β-HCH, γ-HCH and δ-HCH and the code HCHs has been used to denote the sum of these four HCH fractions in literature. DDTs and HCHs are highly resistant to degradation and therefore they have been listed as persistent organic pollutants (POPs).

The Pearl River Delta in the southern China region is one of the global hotspots in terms of environmental contamination of POPs [13–17]. This area has a long history of agricultural application of substantial amounts of organochlorine pesticides, including DDT and HCH until their official ban in 1983 [16]. It is also likely that input of fresh DDT and HCH has continued since 1983 as a result of illegal uses of organochlorine pesticides and the legally permitted applications of DDT-containing dicofol and lindane [15,18].

The dyke-pond integrated cropping and aquaculture system (DPICAS) has been long practiced in the Pearl River Delta [19]. Fishponds were constructed by digging pits in the low-lying areas. The excavated soils were placed in the areas between the fishponds to raise the elevation of the land surface and form the dykes. Traditionally, the dykes were used for growing mulberry trees to provide leaves for silk worm farming and the ponds were used for polyculture of carps with various feeding and spatial niches, leading to efficient utilization of nutrients and space in the ponds [20]. Advances in dyke-pond system technology have focused on crop diversification and animal husbandry [21], which involves cultivation of paddy rice, sugarcane, vegetable, fruit trees, decorative plants and grasses on the dyke. Most of the harvested dyke crops are used to feed the fish as well as livestock, which produce manure to fertilize the pond water to support plankton growth and conse-

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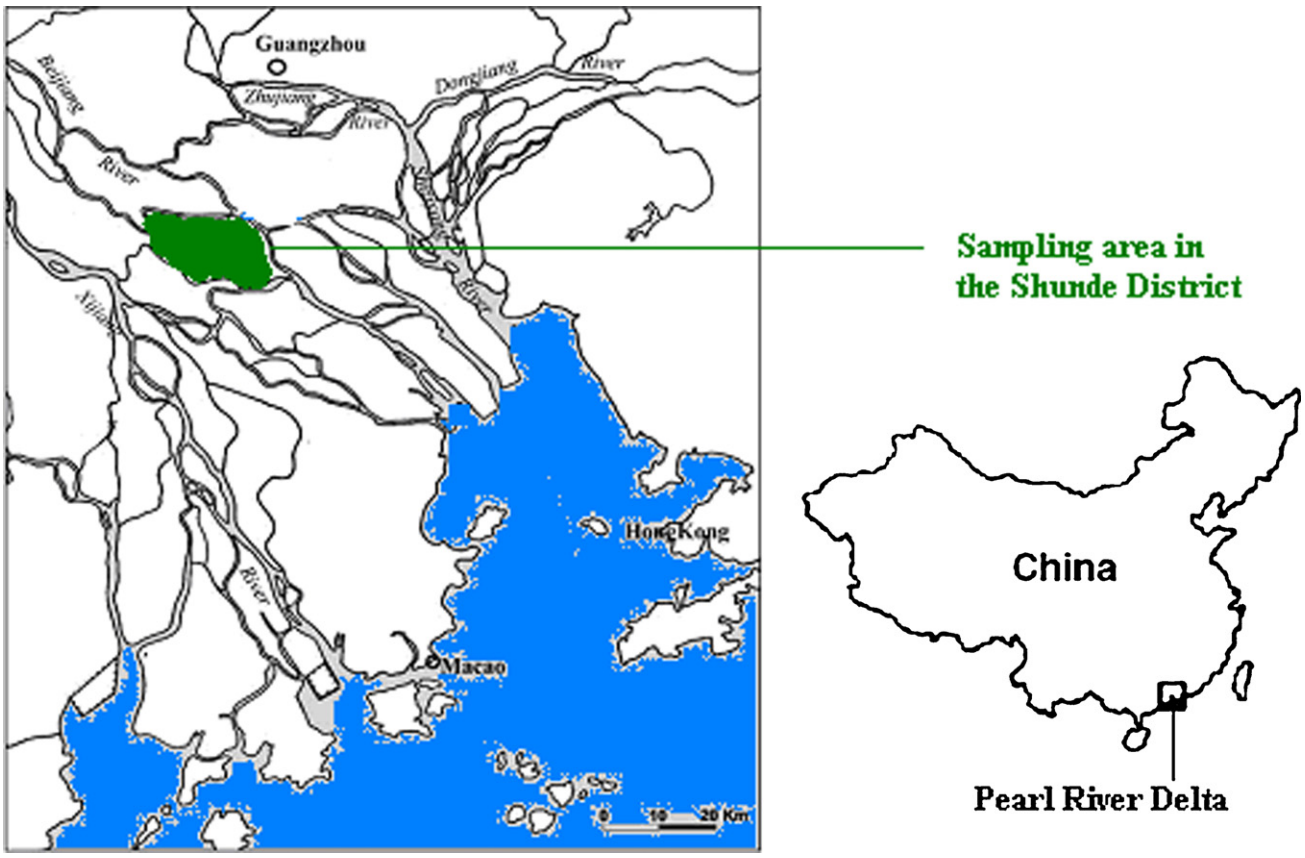

Fig. 1. Map of the Pearl River Delta showing the fishpond sediment sampling area.

quently provide food for the fishes. After the fishes are harvested, the nutrient-enriched bed sediments of the pond are dredged and put on the top of the dyke to maintain a high level of fertility in the dyke soils.

The fishponds in the Pearl River Delta dyke-pond areas are likely to act as a sink for agricultural contaminants due to its lowlying nature. The organochlorine compounds present in the fishpond bottom sediments could have adverse impacts on aquatic life within the ponds, as well as the dyke crops when the sediments are used for formulating topsoil layer on the dyke. In a study on POPs in the fishponds in the non-traditional dyke-pond areas of the Pearl River Delta, Kong et al. [22] found that the fish in the investigated ponds contained elevated levels of DDTs. However, there has been so far no detailed research work conducted to investigate the organochlorine pesticide residues in the benthic sediments of the traditional dyke-pond system and their off-pond impacts after the organochlorine compound-containing pond sediments are used to fertilize the dyke soils.

This article reports on the characteristics of DDTs and HCHs in the fishpond sediments in the study area with a focus on the understanding of the environmental fate of the sediment-borne DDTs and HCHs following the use of the sediments as plant growth media.

2. Materials and methods

2.1. DDT and HCH characterization

2.1.1. Study area

The study site, Shunde District (Fig. 1) of the Foshan City, is located in the central part of the Pearl River Delta, covering an area of about 806 km^2. The area experiences subtropical monsoon climate with an average annual rainfall of 1649 mm. Shunde District is the core area of the integrated dyke-pond system in the Pearl River Delta with a total area of 190 km^2 being used for freshwater aquaculture production at the time when this study was carried out [23].

2.1.2. Sample collection and pretreatment

Fieldwork was carried out during the period from April to May, 2005. Benthic sediments were collected from 11 locations across the entire study area. At each location, a representative pond was selected for sample collection. Five to eight grab samples (0–20 cm) were taken from different spots within a pond using a soil sampler. An approximately equal amount of each grab sample from the same pond was thoroughly mixed to form a composite sample to represent each pond.

In the laboratory, the sediment samples were dried in a vacuum-freeze dryer. The freeze-dried sample was then crushed and stored in a glass bottle that was placed in a fridge with the temperature set at 4 °C prior to sample analysis. Immediately before sample analysis, the samples were re-dried using a vacuum-freeze dryer and ground to pass a 80 mesh sieve.

2.1.3. Environmental risk assessment criteria

The degree of DDT and HCH pollution in the sediments was evaluated by the single pollution index (P_i) [24] and Nemerow composite index (P_N) [25]. The single pollution index (P_i) was obtained by the following formula:

$$P_i = \frac{C_i}{S_i}$$

where C_i represents the observed concentration of DDT; S_i stands for the target concentration of DDT. Four pollution categories are defined: (1) non-pollution ($P_i \leq 1$), (2) slight pollution ($1 < P_i \leq 2$), (3) medium pollution ($2 < P_i \leq 3$) and (4) heavy pollution ($P_i > 3$).

The Nemerow composite index (P_N) was calculated using the following equation:

$$P_N = \left[\frac{(P_{i(\text{ave})}^2 + P_{i(\text{max})}^2)}{2}\right]^{1/2}$$

where $P_{i(\text{ave})}$ and $P_{i(\text{max})}$ stand for the average single pollution index and the maximum single pollution index. Four pollution categories are defined: (1) non-pollution ($P_N \leq 0.85$), (2) slight pollution ($0.85 < P_N \leq 1.71$), (3) medium pollution ($1.71 < P_N \leq 2.56$) and (4) heavy pollution ($P_N > 2.56$).

The ecological risk assessment of the sediment-borne DDTs was made using the criteria ERL (effect range-low) and ERM (effect range-median) recommended by Long et al. [26]. When the observed DDTs concentration is below ERL, the toxic risk is viewed as <10% while the toxic risk is expected to be >50% when the observed DDTs concentration is higher than ERM.

2.2. Microcosm experiment

2.2.1. The experimental soil

The benthic sediment in one of the eleven investigated ponds (located in Zhongchong Village, Leliu Town) was selected to formulate experimental soils for the microcosm experiment. This was to examine the environmental fate of DDTs and HCHs after the fishpond sediment was used as growth media for vegetable production. About 1000 kg of the bed sediment were collected from a depth of 0–30 cm after emptying the pond water. The sediment materials collected were air-dried and crushed to pass a 5 mm sieve before being used as the experimental soil for the microcosm experiment. The sediment sample had a pH of 4.22 and an organic matter content of 2.26%. Total N, P and K were 1.890, 0.516 and 4.335 g kg^{-1} respectively. Available N, P and K were 0.312, 0.072 and 1.270 g kg^{-1}, respectively.

2.2.2. The test plant

Ipomoea aquatica, a vegetable plant species that is commonly grown on the fishpond dyke, was used as the test plant in the microcosm experiment.

2.2.3. Experimental design

The microcosm experiment was conducted in a growth house equipped with temperature and light intensity controllers. One control and one treatment were set for the experiments: (1) control (C): pond sediment-turned soil only; (2) treatment (T): pond sediment-turned soil cultivated with the vegetable. The experiment was performed in 4 replicates.

Five kilograms of the experimental soil were put into each pot (height: 17 cm; inner diameter at the base: 20 cm; inner diameter at the top: 27 cm). Prior to seed sowing in the treatment, the soils in both the control and the treatment were incubated for 7 days with the soil moisture controlled at field capacity. The growth experiment commenced on November 20, 2005. The pots were placed in the growth house randomly with temperature set at 27 ± 1 °C. 14 seeds were then sown in each pot. After 10 days following seed sowing, 8 healthy seedlings were selected to remain in each pot. The plants were exposed to a photoperiod of 8 h with light intensity set at 12000Lux each day during the entire period of the experiment.

During the period of growth experiment, 200 mL of deionized water were added to each pot daily. Leachate was collected from the bottom of each pot daily for chemical analysis. The water samples were stored at 4 °C in a fridge prior to analysis.

Soil samples were taken from each pot on the 1st, 12th, 22nd and 35th day after seed sowing. For each pot, 5–7 sub-samples of soil were collected using a soil sampler. The sub-samples were then mixed thoroughly to form a composite sample (approximately 200 g). The composite soil samples were air-dried, ground to pass a 0.25 mm sieve and stored at 4 °C in a fridge prior to chemical analysis.

On the 35th day of the experiment, the whole plant was harvested, washed and oven-dried at 55 °C. The oven-dried plant residue from each pot was then weighed and finely ground prior to analysis.

2.3. Sample extraction and analytical methods

Various DDT and HCH isomers in the sediment, soil, water and plant tissue samples were extracted, cleaned up and analyzed using modified procedures documented in US EPA Method 3500 series, Method 3600 series and Method 8081 [27–29].

For extraction of various DDT and HCH isomers from the sediment and soil samples, a Soxhlet method was employed. 20 g of the freeze-dried sediment or soil were placed inside a thimble made from filter paper, which was loaded into the main chamber of the Soxhlet extractor. The sediment or soil sample was soaked with 30 mL of mixed acetone and petroleum ether solution (mixing ratio: 1:1) for 12 h. The Soxhlet extractor was then placed onto a distillation flask containing 70 mL of 1:1 acetone:petroleum ether mixture. Soxhlet extraction was allowed to proceed for 4 h with the water bath temperature being maintained at between 62 and 64 °C and the cooling water temperature being controlled at around 10 °C. The extract was then purified with 2% sodium sulfate and concentrated sulfuric acid in a separatory funnel and passed through a funnel containing anhydrous sodium sulfate. The purified extract was collected in a flask and the volume of the extract was reduced to 5 mL by a rotary evaporator prior to analysis.

For extraction of water-borne DDT and HCH isomers, 200 mL of water sample was spiked with 25 mL of petroleum ether solution and shaken on a rotary shaker for 10 min. The content was then transferred to a separatory funnel and the water was decanted. Sample purification was performed by repeated treatment of the sample with concentrated sulfuric acid and then 2% sodium sulfate and passed through a funnel containing anhydrous sodium sulfate. The purified extract was collected in a flask and the volume of the extract was reduced to 10 mL by a rotary evaporator prior to analysis.

For extraction of plant tissue-borne DDT and HCH isomers, 3 g of dried plant sample was soaked with 80 mL of mixed acetone and petroleum ether solution (mixing ratio: 1:1) for 12 h, followed by ultrasonic extraction for 30 min. The content was passed through a funnel containing anhydrous sodium sulfate and active carbon. The filtrate was then transferred to a separatory funnel, followed by adding 100 mL of 2% sodium sulfate to remove acetone. The volume of the extract was reduced to 2 mL by a rotary evaporator. Sample cleanup was performed by a Florisil column method.

All extracts were analyzed using an Agilent HP-6890N GC-ECD system with a HP-5 fused-silica capillary column (30 m × 0.25 mm I.D × 0.25 μm). Helium was used as the carrier gas at 2 mL min^{-1} and nitrogen was used as the make-up gas 60 mL min^{-1}. The oven temperature began at 165 °C for 2 min and increased to 265 °C (2 min hold time) at a rate of 6 °C min^{-1}. Splitless injection of a 2 μL sample was performed. Injector and detector temperatures were maintained at 210 and 320 °C, respectively.

2.4. Quality control and quality assurance

2,4,5,6-Tetrachloro-m-xylene was selected as the surrogate for recovery test. The surrogate and stock standard solutions of various DDT and HCH isomers were purchased from Supelco. The surrogate was added to each sample, blank, laboratory control sample and matrix spike sample immediately prior to pesticide extrac-

Table 1
Mean concentration and range of various DDT and HCH fractions in the benthic sediments collected from 11 representative fishponds in the Shunde District, Pearl River Delta.

Organochlorine	Fraction or fraction ratio	Mean (ng g^{-1})	Range (ng g^{-1})	Isomer percentage
DDTs		30	10–87	–
	o,p′-DDT	15	3.8–23	47
	p,p′-DDT	9.7	2.3–43	32
	p,p′-DDE	2.3	0.93–8.3	7.8
	p,p′-DDD	3.8	1.3–14	12
	DDT/DDE + DDD	4.4	2.9–6.3	
	o,p′-DDT/p,p′-DDT	2.1	0.53–3.1	
	DDD/DDE	1.7	0.78–2.7	
HCHs		61	15–138	–
	α-HCH	36	0.84–63	62
	β-HCH	4.7	udl–15	8.1
	γ-HCH	1.7	udl–5.1	3.6
	δ-HCH	19	udl–98	26

tion. The recoveries of surrogate standards ranged from 80.71% to 95.32%.

The detection limit of DDT isomers ranged from 0.03 ng g^{-1} to 0.15 ng g^{-1} and the recoveries of DDT in the matrix spike samples ranged from 88.7% to 104%. The detection limit of HCH isomers ranged from 0.03 ng g^{-1} to 0.10 ng g^{-1} and the recoveries of HCH in the matrix spike samples ranged from 78.32 to 90.56%. The relative standard deviation (RSD) of replicate samples for both DDTs and HCHs in the soil and plant tissue samples was all <15%. Since the volume of leachate from each growth chamber was not sufficient for analysis. A composite sample was formed for each treatment by combining the leachate sub-samples from all replicates. Consequently, no RSD was obtained for the water samples.

2.5. Statistical analysis

The statistical significance of difference between treatment means was determined by Duncan's multiple range test.

3. Results and discussion

3.1. Characteristics of DDTs and HCHs

The mean concentration and range of various DDT and HCH fractions, as well as the total DDT (DDTs) and total HCH (HCHs) are given in Table 1. The concentration of DDTs ranged from 10 to 87 ng g^{-1} with a mean value of 30 ng g^{-1}. On average, the DDT fractions in the sediments were in the following decreasing order: o,p′-DDT > p,p′-DDT > p,p′-DDD > p,p′-DDE. HCHs had a mean concentration of 61 ng g^{-1} with a range of 15–138 ng g^{-1}. On average, various HCH isomers in the sediments were in the following decreasing order: α-HCH > δ-HCH > β-HCH > γ-HCH.

Kong et al. [22] reported various DDT fractions in fishpond sediments collected from other parts (non-typical dyke-pond areas) of the Pearl River Delta, including Zhuhai, Zhongshan, Guangzhou, Dongguan and Hong Kong. In general, these fishponds had the benthic sediments with lower concentration of DDTs than those in the pond sediments investigated in the current study. Comparison with the estuarine sediments [17] also reveals a higher mean DDTs value for the pond sediments in this study, relative to that in the sediments in the Daya Bay.

The fishpond sediment-borne DDTs may be mainly derived from dyke runoff, river water that is used to compensate the loss of pond water due to evaporation, atmospheric deposition and fish feed added into the ponds. It is likely that surface runoff from the dyke soils plays a major role in providing DDTs for the ponds given its closest proximity to the ponds and possibly high dose of DDT application for intensive cropping. Li et al. [15] found that the mean concentration of DDTs in the paddy rice soils and dryland soils in the Pearl River Delta were about 47 and 56 ng g^{-1}, respectively. These DDTs values are much higher than that in the agricultural soils of Hong Kong [28] where very low concentration (4.32 ng g^{-1}) of DDTs was found in the fishpond sediment [22].

The ratios of DDT/DDE + DDD, o,p′-DDT/p,p′-DDT and DDD/DDE have been widely used to characterize DDTs in various environmental compartments [15,22]. A DDT/DDE + DDD value >1 indicates the presence of a fresh input of DDT into the environmental system of concern [15]. The average DDT/DDE + DDD of the pond sediments in this study was over 4 (Table 1). While this result generally supports many authors' view that there have been fresh inputs of DDT in the Pearl River Delta region [16], it is realized that many other factors may contribute to such a high DDT/DDE + DDD value. Unlike agricultural lands, fishponds are not target sites for direct application of DDT. The status of fishpond sediment-borne DDTs reflects the mixture of DDTs from multiple sources. It is not expected that various fractions of DDTs in the dyke soils be washed off and enter the pond proportionally given that different DDT fractions have different mobility in soils, as affected by their affinity to soil colloids and solubility in soil pore water. The mean o,p′-DDT/p,p′-DDT of the investigated pond sediments was >2 (Table 1), which was much higher than that for technical DDT (frequently < 0.3 [30]). This may be partly attributed to the different mobility rate between the two DDT isomers in the dyke soils. Since o,p′-DDT has a higher water solubility than does p,p′-DDT [30], it is therefore likely that more o,p′-DDT than p,p′-DDT was leached from the dyke soils into the fishpond. Nevertheless, the much higher o,p′-DDT/p,p′-DDT, relative to that for technical DDT, appears to suggest that the o,p′-DDT-dominated dicofol was a likely source of fresh DDT in the study area. The predominance of DDD over DDE, as indicated by a high DDD/DDE (1.7, refer to Table 1) reflects that the metabolism of DDT was largely through anaerobic degradation, which is in agreement with the expected reducing environments that are encountered in the fishpond bottoms.

There were close interrelationships among p,p′-DDT, p,p′-DDD and p,p′-DDE for the 11 investigated sediment samples (Fig. 2a–c), suggesting that the magnitude of DDT influx has important control on the amount of DDT metabolites present in the sediments. While p,p′-DDT is also related to o,p′-DDT, their relationship was less close, as compared to those among p,p′-DDT, p,p′-DDD and p,p′-DDE. This may be attributed to variation on dicofol-originated DDT influx among different sites.

Technical HCH typically contains 65–75% of α-HCH, 5–6% of β-HCH, 13% of γ-HCH and 6% of δ-HCH [15]. It is interesting to note that the investigated pond sediments have a much higher mean percentage of δ-HCH and a much lower mean percentage of γ-HCH, compared to the technical HCH despite that lindane (99% of γ-HCH) is the most likely source of the fresh HCHs in this area [31]. γ-HCH is known to be more soluble and degradable, compared to other

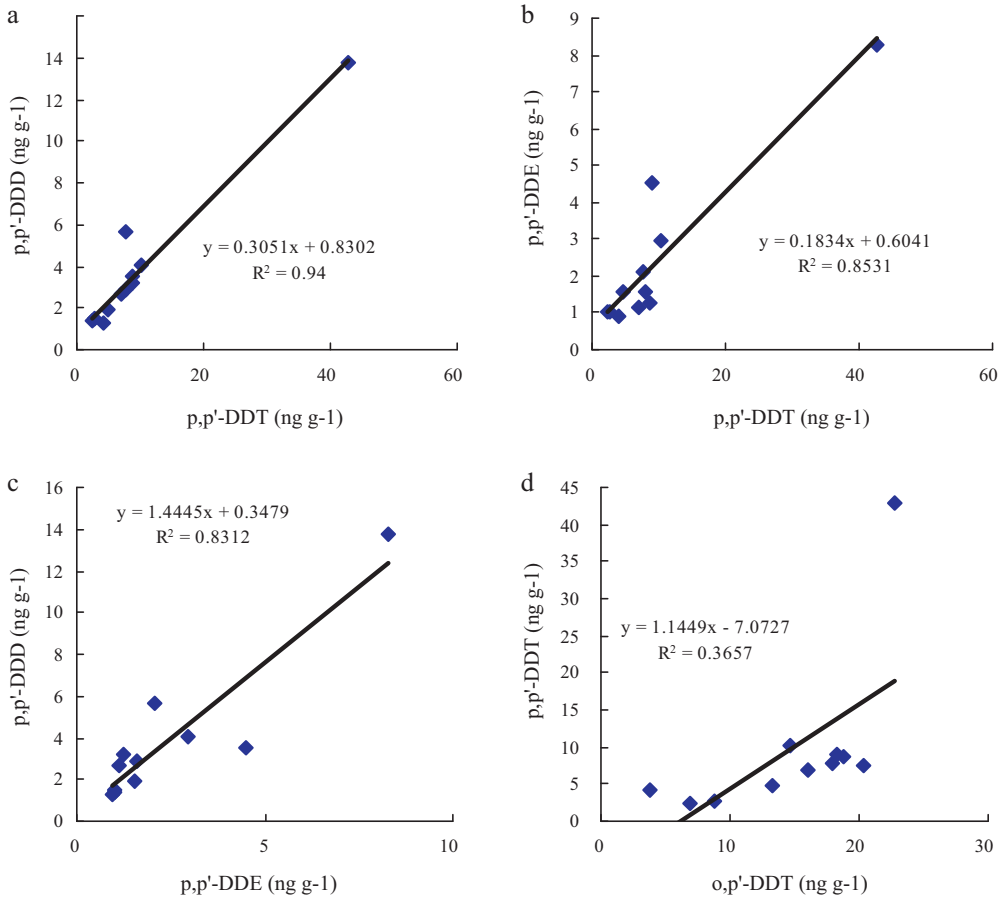

Fig. 2. Relationship between (a) p,p′-DDT and p,p′-DDD, (b) p,p′-DDT and p,p′-DDE, (c) p,p′-DDE and p,p′-DDD, and (d) o,p′-DDT and p,p′-DDT in the investigated fishpond bed sediments.

isomers [15,32]. Conversion of γ-HCH to α-HCH and δ-HCH has been suggested [33]. It is likely that the higher solubility of γ-HCH in water may weaken its capacity to compete with other HCH isomers and other organic compounds such as DDTs for the available adsorption sites in the pond sediments. This, in combination with the phase transformation and possible volatilization/evaporation loss may be responsible for the observed low concentration of γ-HCH in the pond sediments. Both technical HCH and lindane contain only small amounts of δ-HCH. Therefore, the enrichment of δ-HCH in the pond sediments is likely to be the result of γ-HCH-δ-HCH conversion and the extremely high stability of δ-HCH [34] allows it to accumulate in the sediments.

3.2. Environmental risk assessment

Pollution assessment using single pollution index (P_i) [24] reveals that for HCHs, about 9, 46 and 45% of the sediment samples fell into medium pollution, slight pollution and non-pollution categories, respectively; for DDTs, about 9 and 91% of the samples fell into slight pollution and non-pollution categories, respectively (Table 2). By comparison, the HCH pollution was more severe than DDT pollution for the investigated sediment samples.

By using Nemerow composite index (P_N) [25] to assess the combined effect of both HCH and DDT pollution. The results return that about 9, 64 and 27% of the investigated samples fell into medium pollution, slight pollution and non-pollution categories, respectively (Table 2).

Ecological risk assessment of DDT using the method of Long et al. [26] reveals that there were 91% of the samples that had DDTs value between ERL and ERM with the remaining 9% of the samples having the DDTs value above ERM (Table 2). Based on the above analysis, it is considered that the fishpond sediment-borne DDTs posed an environmental threat to the pond ecosystem in the study area.

The guideline values of ERL and ERM were not established for HCHs. The Canadian sediment quality guidelines for the protection of aquatic life [35] established two similar guideline values:

Table 2
Pollution indices of DDTs and HCHs, and ecological risk assessment of DDTs in the investigated fishpond sediments in the Shunde District.

Sample No.	Single pollution index (P_i)		Nemerow composite index (P_N)
	HCHs	DDTs	
YT1	0.88	1.75	1.55
YT2	1.00	0.64	0.91
YT3	1.14	0.54	1.00
YT4	0.88	0.61	0.81
YT5	0.93	0.71	0.88
YT6	1.47	0.70	1.29
YT7	1.99	0.20	1.61
YT8	2.78	0.23	2.23
YT9	0.30	0.64	0.56
YT10	1.04	0.43	0.90
YT11	0.95	0.28	0.80

Assessment criteria	
ERL (ng g^{-1})	1.58
ERM (ng g^{-1})	46.1
<ERL (%)	0
ERL–ERM (%)	91
>ERM (%)	9

Table 3
Changes in soil DDTs and HCHs during the period of the plant growth experiment.

Parameter		1st day	12th day	22nd day	35th day
DDTs ($ng\,g^{-1}$)	C	71.1 ± 6.00	71.0 ± 9.89 a	45.5 ± 7.66 b	44.4 ± 4.90 a
	T	71.1 ± 6.00	76.6 ± 4.30 a	61.2 ± 8.37 a	49.1 ± 6.44 a
HCHs ($ng\,g^{-1}$)	C	133 ± 6.96	129 ± 5.58 b	71.1 ± 17.1 a	28.1 ± 7.83 a
	T	133 ± 6.96	140 ± 6.44 a	80.3 ± 19.3 a	27.6 ± 3.33 a

Table 4
Mass balance of DDTs and HCHs in the microcosm system (unit: μg).

Organochloride	Plant uptake	Soil retention	Leaching	Unaccounted loss
DDT	0.018 (0.00005%)	233 (69.11%)	0 (0%)	104 (30.89%)
HCH	0.043 (0.00007%)	131 (19.77%)	8.23 (1.24%)	523 (78.98%)

(a) interim freshwater sediment quality guideline concentration (ISQG) and (b) probable effect level (PEL) for a range of pollutants, including lindane (γ-HCH). However, total HCH and other HCH isomers were not considered in the Canadian system. The ISQG and PEL values for lindane in freshwater sediments are 0.94 and 1.38 $ng\,g^{-1}$, respectively. Consequently, about 46% of the investigated fishpond sediments had lindane concentration above the probable effect level. The sediments with lindane concentration below ISQG and between ISQG and PEL accounted for 27% each. These results suggest that sediment-borne lindane alone posed a potential threat to aquatic life in the fishponds.

It is important to note that lindane only accounted for a very small proportion of HCHs in the investigated fishpond sediments (3.6%). Therefore, the ecological risk of HCHs could be far more remarkable.

3.3. Fates of DDTs and HCHs following the use of the sediment as plant growth media

No DDTs were detected from any of the leachates collected from the control and the treatment during the period of the experiment. This suggests that the sediment-borne DDTs was tightly bound by the sediment-turned soil and leaching of DDTs with percolating water is negligible. The leachate collected on the first day of the experiment contained nearly 6 and 8 $ng\,mL^{-1}$ of HCHs for the control and the treatment, respectively. HCHs then decreased over time and only trace amounts of HCHs were detected on the 32nd day of the experiment (Fig. 3).

Variation on concentration of DDTs and HCHs in the soil during the period of the experiment can be seen from Table 3. There was no statistically significant difference in the residual DDTs and HCHs between the control and the treatment except for the samples collected on the 22nd day for DDTs and on the 12th day for HCHs. In general, the variation in both DDTs and HCHs in the soils was small during the earlier part of the experiment (1st–12th day). Marked decrease in DDTs and HCHs occurred after the 12th day.

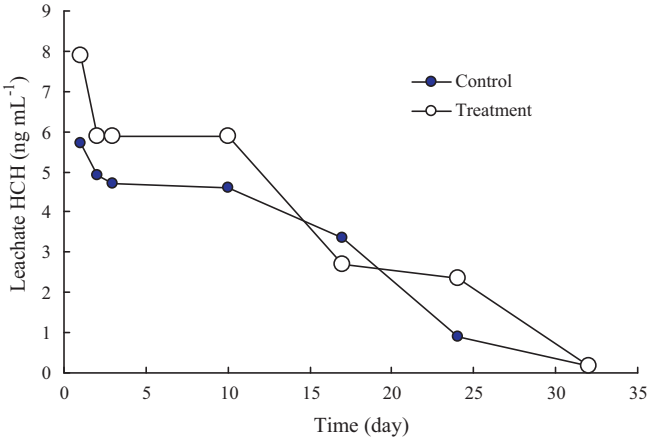

Fig. 3. Changes in leachate HCHs during the period of the experiment.

In comparison, the soil experienced a rapider loss in HCHs than in DDTs. This is in agreement with the general belief that HCHs have a higher mobility than do DDTs in soils [36].

The DDTs and HCHs uptake by the plant only accounted for a very small proportion (0.00005% for DDTs and 0.00007% for HCHs) of the plant–soil–water system. The mass balance of DDTs and HCHs for the microcosm experiment is shown in Table 4. For DDTs, over 2/3 of the original soil-borne DDTs was retained in the soil on the last day (the 35th day) of the experiment while <1/3 of the original soil-borne DDTs was lost possibly due to microbial degradation since volatilization and evaporation of DDTs from soils are usually weak and no leaching loss was recorded for the experiment. For HCHs, only <20% of the original soil-borne HCHs was retained in the soil on the 35th day of the experiment while leaching loss accounted for 1.24% and unaccounted loss took up nearly 79% of the original soil-borne HCHs. However, certain amounts of HCHs might disappear as a result of volatilization and evaporation in addition to degradation as HCHs are more volatile, relative to DDTs.

4. Conclusion

It is likely that fresh input of DDT from the substantial application of dicofol in the study area has markedly affected the status of the fishpond sediment-borne DDTs. DDT degradation for the investigated sediments was mainly through anaerobic decomposition. It is not certain why the investigated pond sediments have a much higher mean percentage of δ-HCH and a much lower mean percentage of γ-HCH, compared to the technical HCH despite that lindane (99% of γ-HCH) is the most likely source of the fresh HCHs in this area. Perhaps the higher solubility of γ-HCH in water may weaken its capacity to compete with other HCH isomers and other organic compounds. This, in combination with the phase transformation and possible volatilization/evaporation loss may be responsible for the observed low concentration of γ-HCH in the pond sediments. The enrichment of δ-HCH in the pond sediments is likely to be the result of γ-HCH-δ-HCH conversion and the extremely high stability of δ-HCH allows it to accumulate in the sediments.

The levels of both DDTs and HCHs were higher in the investigated pond sediments, compared to those in the estuarine sediments and previously reported pond sediments in non-traditional dyke-pond system. The fishpond sediment-borne DDTs and HCHs posed an environmental threat to the pond ecosystem in the study area.

Upon the use of the sediment as plant growth media under the experimental conditions set in this study, the majority of soil-borne DDTs was retained in the soil while <1/3 of the original soil-borne

DDTs was lost possibly due to microbial degradation; no leaching loss was recorded and only a very small amount of DDT was lost through plant uptake. For HCHs, only <20% of the original soil-borne HCHs was retained in the soil while leaching loss accounted for 1.24% and nearly 79% of the original soil-borne HCHs disappeared as a result of HCHs degradation and possibly volatilization and evaporation.

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