Effects of Different Fertilizers on Soil-borne DDTs Dynamics and Its Impacts on DDTs Uptake by *Ipomoea aquatica*

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Abstract
A pot experiment was conducted to examine the effects of.various fertilizers on the dynamics of soil-borne DDTs and their subsequent impacts on DDTs uptake by a test plant. The results show that there was a significantly lower soil residual DDTs concentration in the iron-rich fertilizer-treated soil than in other fertilizer-treated soils. However, all the non-iron-rich fertilizers showed no significant effect on the reduction of soil DDTs on the last day of the experiment, as compared to the control. There was a close relationship between the soil residual DDTs and plant tissue DDTs. This suggests that the uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs. Application of iron-rich fertilizer enhanced the degradation of the soil DDTs and subsequently reduced the uptake of DDTs by the test plant. The findings obtained from this study have implications for remediation of DDTs-polluted soils.

Key Words
Fertilizer, DDT, pesticide, soil contamination, plant uptake.

Introduction
The extensive application of dichlorodiphenyltrichloroethane (DDT) for pest control prior to the global restriction on its use resulted in widespread presence of this synthesized chemical and its metabolites, dichlorodiphenyldichloroethane (DDD) and chlorodiphenyldichloroethylene (DDE) (DDTs is frequently used to stand for the sum of DDT, DDD and DDE) in the environment (Longnecker, 2005). The Pearl River Delta in the southern China region is one of the global hotspots in terms of environmental contamination of persistent organic pollutants (POPs). This area has a long history of agricultural application of substantial amounts of organochlorine pesticides, including DDTs until their official ban in 1983 (Zhang *et al*. 2007). It is also likely that input of fresh DDTs has continued since 1983 as a result of the application of DDT-containing dicofol (Qiu *et al*. 2005).

The dyke-pond integrated cropping and aquaculture system has been long practiced in the Pearl River Delta (Ruddle *et al.* 1983). The fishpond sediments are potential sinks for DDTs and the sediment-borne DDTs could have adverse impacts on the quality of crop products due to elevated DDTs level in the plant tissues when the DDT-containing sediments are used for formulating topsoil layer on the dyke, which forms part of the routine operation in the dyke-pond system (Edwards 2008). The rate of DDT degradation in soils varies with environmental conditions, which could be affected by fertilizer applications. The objective of this work was to understand the effects of different fertilizer types on the dynamics of soil borne DDTs and subsequently the impacts on plant uptake of DDTs.

Materials and Methods
A representative fishpond located in the Shunde District of Foshan City was selected for this study. 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 pot trial. 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 respectively. Available N, P and K were 0.312, 0.072 and 1.270 g/kg, respectively. The original soil contained 71 ng/g of DDTs. Prior to the growth experiment, an appropriate amount of technical DDT was added to the soil to simulate an on-farm application of DDT to raise the soil DDTs level to a theoretical concentration of DDT to 190 ng/g. A DDTs concentration of 186 ng/g was recorded on th 7th day of the pre-experiment incubation period.

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

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The four types of fertilizers used for different treatments are (1) organic fertilizer (chemical composition: 19.5 g/kg of nitrogen; 2.5 g/kg of phosphorus; 55.6 g/kg of K) , (2) compound fertilizer (chemical composition: 59.9 g/kg of nitrogen; 10.1 g/kg of phosphorus; 53.5 g/kg of K), (3) inorganic fertilizer and (4) Iron-rich trace element fertilizer (chemical composition: 40.3 g/kg of nitrogen; 6.7 g/kg of phosphorus; 58.6 g/kg of K; 1.9 g/kg of Fe^{2+}). No DDTs were detected from the fertilizers used in this experiment.

The experiment was conducted in a growth house equipped with temperature and light intensity controllers. Two controls and four treatments were set for the experiments: (1) Control 1 (C1): pond sediment only; (2) Control 2 (C2): pond sediment cultivated with vegetable; (3) Treatment 1 (T1): pond sediment with added organic fertilizer and cultivated with vegetable; (4) Treatment 2 (T2): pond sediment with added compound fertilizer and cultivated with vegetable; (5) Treatment 3 (T3): pond sediment with added inorganic fertilizer and cultivated with vegetable; and (6) treatment 4 (T4): pond sediment with added iron-rich trace element fertilizer and cultivated with vegetable. The experiment was performed in 4 replicates.

In each pot (height: 17 cm; inner diameter at the base: 20 cm; inner diameter at the top: 27 cm), 5 kg of the experimental soil was mixed with a relevant fertilizer. The pots were placed in the growth house randomly with temperature set at $27\pm1^{o}C$. 14 seeds were then sown in each pot. The plants were exposed to a photoperiod of 8 hours with light intensity set at 12000Lux each day during the entire period of the experiment. After 10 days following seed sowing, 8 healthy seedlings were selected to remain in each pot. Soil samples were taken from each pot on the 1^{st}, 10^{th}, 20^{th} and 30^{th} 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 $4^{o}C$ in a fridge prior to chemical analysis.

On the 30th day of the experiment, the whole plant was harvested, washed and oven-dried at $55^{o}C$. The oven-dried plant residue from each pot was then weighed and finely ground prior to analysis.

DDTs in the soil and plant tissue samples were extracted using the procedures described in US EPA3510B (US EPA 1994) and measured 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.

The detection limit ranged from 0.03 ng g^{-1} to 0.15 ng g^{-1} and the recoveries of surrogate standards ranged from 88.7 to 104%. The relative standard deviation (RSD) of replicate samples were less <15%. The statistical significance of difference between treatment means was determined by Duncan's multiple range test.

Results and Discussion

Change in soil-borne DDTs for the controls and treatments during the period of experiment can be seen from Figure 1. There was a trend that DDTs concentration decreased over time. After 10 days of growth experiment, approximately 45-55% of DDTs disappearred from the soils; there was a significant difference in residual soil DDTs ($P<0.05$) between C1 (pond sediment only) and C2 (pond sediment cultivated with vegetable) or any treatment; C1 had the highest concentration of soil-borne DDTs among the controls and treatments. There was no significant difference in residual soil DDTs ($P>0.05$) between C2 and T2 (pond sediment with added compound fertilizer and cultivated with vegetable), which had significantly higher ($P<0.05$) DDTs than the remaining three treatments i.e. T1 (pond sediment with added organic fertilizer and cultivated with vegetable), T3 (pond sediment with added inorganic fertilizer and cultivated with vegetable) and T4 (pond sediment with added iron-rich trace element fertilizer). These latter three treatments showed no significant significance in soil-borne DDTs among each others. On the 20^{th} day of the experiment, there was no statistically significant difference in residual soil DDTs ($P>0.05$) among all the controls and treatments despite that the mean concentration of soil DDT varied markedly among each others.

At harvest (the 30^{th} day of the experiment), T4 had the lowest residual concentration of DDTs (statistically significant at $P<0.05$) in the soil among all the controls and treatments. There was no significant difference ($P>0.05$) in residual DDTs in the soil among C2, T1 and T2, which had significantly lower soil DDTs, compared to C1 and T3.

There was no significant difference (P>0.05) in residual DDTs in the soil between C1 and T3. Compared to the first 10 days, the decrease in soil residual DDTs was relatively slower during the period from the 10th to 30th day of the experiment (Figure 1). Since DDT is not subject to water leaching and volatilization, it is likely that the loss of soil DDTs during the period of the experiment was mainly through degradation. The observed significantly lower soil residual DDTs in the iron-rich fertilizer-treated soil than in other fertilizer-treated soil generally agrees with previous work done by other authors that showed catalyzed degradation of DDT by reduced forms of iron (e.g. Boussahel *et al*. 2006). However, no significantly different (P>0.05) effect on the reduction of soil-borne DDTs by any non-iron-rich fertilizers was observed on the last day (30th day) of the experiment, as compared to the control (C2). As a matter of fact, the inorganic fertilizer treatment even resulted in a higher residual concentration of DDTs, relative to the control (Figure 1).

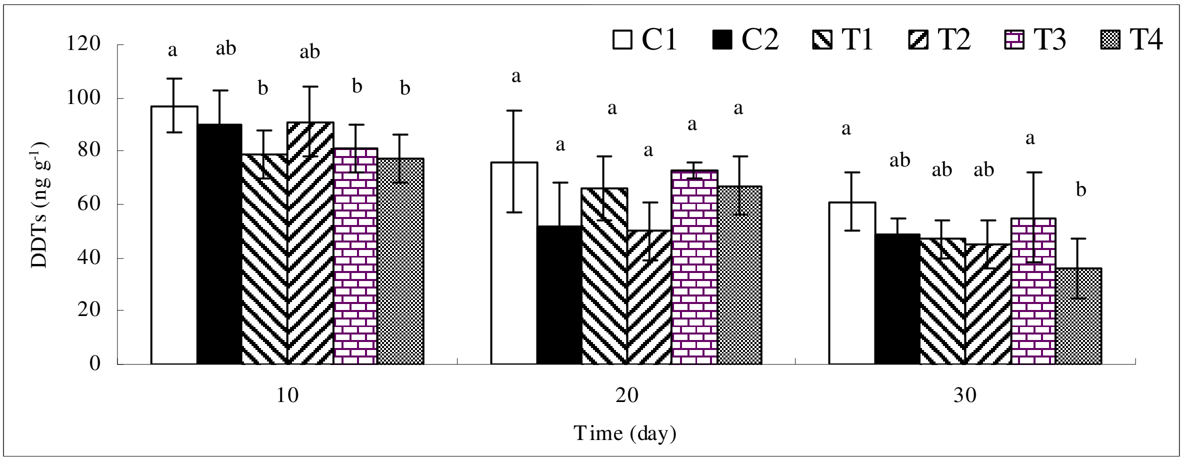

Figure 1. Change in soil-borne DDTs for the controls and treatments during the period of experiment

The concentration of tissue DDTs in *Ipomoea aquatica* at harvest is shown in Figure 2. There was a significant (P<0.05) difference among the control and various treatments. The mean concentration of plant tissue DDTs for the control and various treatments was in the following decreasing order: C2 >T3 > T1 >T2 >T4.

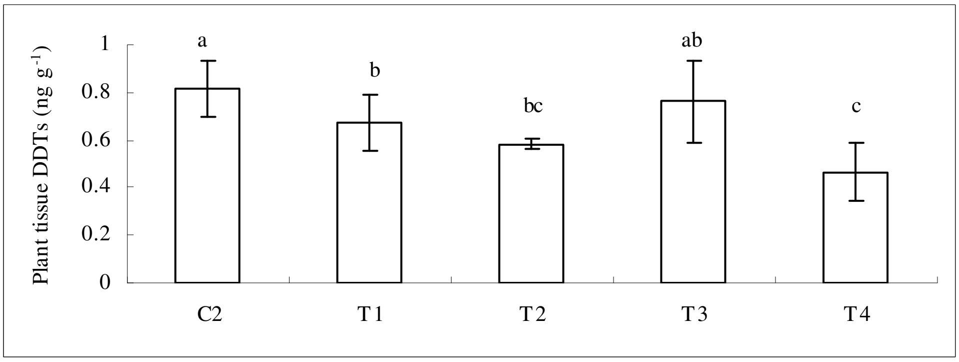

Figure 2. The concentration of tissue-borne DDTs of the Ipomoea aquatica for the control and various treatments at harvest

There was a close relationship between the soil residual DDTs and the plant tissue DDTs at harvest (Figure 3). This suggests that the uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs, i.e. the more residual DDTs the soil contained, the higher concentration of DDTs the plant tissue had.

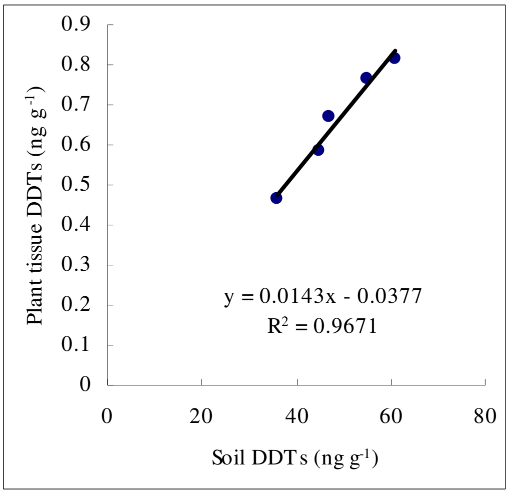

Figure 3. Relationship between soil residual DDTs and plant tissue DDTs at harvest.

The research findings obtained from this study have implications for the management of benthic sediment-turned soils in the dyke-pond integrated cropping and aquaculture production systems. Application of iron-rich fertilizers may enhance the degradation of the soil DDTs and subsequently reduce the uptake of DDTs by the test plant.

Conclusion

There was a significantly lower soil residual DDTs concentration in the iron-rich fertilizer-treated soil than in other fertilizer-treated soil. The uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs. Application of iron-rich fertilizer may enhance the degradation of the soil DDTs and subsequently reduce the uptake of DDTs by plants. The research findings obtained from this study have implications for the management of benthic sediment-turned soils in the dyke-pond integrated cropping and aquaculture production systems.

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