



## Assessment of organochlorine pesticide contamination in relation to soil properties in the Pearl River Delta, China

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### HIGHLIGHTS

- ▶ Residue levels of HCHs and DDTs in soils were mainly controlled by TOC and CFe.
- ▶ Transformations of soil HCHs may be affected by pH and DDT transformation correlated significantly with AFe and CFe.
- ▶ The re-emission potential of OCPs in soils was mainly affected by soil OCP concentrations and land use types.
- ▶ HCHs and DDTs in soils may potentially pose ecological risk to plants and animals.

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### ABSTRACT

High levels of organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) have been found in soil of the Pearl River Delta (PRD), attributable to high pesticide application in this area. Consequently, the occurrence and environmental effect of HCHs and DDTs in the PRD have attracted considerable attention. However, study focusing on the influence of potential factors such as soil property on the environmental fate of HCHs and DDTs in the PRD has been rare. The present study aimed to investigate the impact of soil physiochemical properties on the distribution patterns and fate of soil HCHs and DDTs on a large spatial scale. Levels of HCHs (sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH) and DDTs (sum of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDT), 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDD), and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (*p,p'*-DDE)) in 151 soil samples covering all areas of the PRD and physiochemical parameters related to soil properties including pH, total organic carbon (TOC), total Fe (TFe), DCB-Fe (DFe), amorphous-Fe (AFe), complexed-Fe (CFe), total Mn (TMn), DCB-Mn (DMn), amorphous-Mn (AMn), complexed-Mn (CMn) and cation exchange capacity (CEC) were determined. The residual levels of HCHs and DDTs in soils of the present study, which are mainly controlled by soil TOC and CFe content and varying spatially with land use types, may potentially pose ecological risk to plants and animals. On the other hand, transformation of soil HCHs may be affected by pH and DDT transformation correlated significantly with AFe and CFe. Currently, soil has become an important secondary source of OCPs and the re-emission potential of OCPs in soil was mainly affected by soil OCP concentrations and land use types.

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## 1. Introduction

Soil is the base for terrestrial ecosystems, providing the necessary nutrients and moisture for plants and habitats for soil fauna. Consequently, toxic chemicals, especially persistent organic pollutants in affected soil, presumably resulted from increased anthropogenic activity, can be accumulated in plants or soil fauna, resulting in unexpected risk to the terrestrial ecosystems. Organochlorine pesticides (OCPs), as a class of typical persistent organic pollutants, is still ubiquitous in the

environment currently (Cai et al., 2008), due to their long history of use and difficult degradation. Therefore, examining the occurrence and environmental fate of OCPs in soil bears substantial implications for the terrestrial ecosystems including human. Actually, residual levels and environmental behaviors of OCPs in soil are affected by many factors (Boul et al., 1994). These factors included application history, agricultural practices such as flood irrigation, superphosphate application and tillage (Boul et al., 1994), soil properties such as pH, total organic carbon (TOC) and water content (Boul et al., 1994; Zhang et al., 2006). Beside, soil texture also affects the OCP level in soil. A previous study (Szeto and Price, 1991) found that levels of HCHs and DDTs were higher in organic musk soil than in silt loam soil and loamy sand. Moreover, soil properties can be affected by land use types, therefore variations in land

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use remarkably affect the residue level of organochlorine pesticides (Hao et al., 2008). For example, residual levels of HCHs and DDTs in soil from the Pearl River Delta (PRD) decreased in order of upland crop soil > paddy soil > natural soil (Li et al., 2006). In addition, the degradation of OCPs examined by many previous studies (Wedemeyer, 1967; Quensen et al., 2001; Li et al., 2010) is also an important process occurring in the environment. Previous studies indicated that iron and manganese oxide widely distributed in soils usually involved the transformation of chlorinated organic pollutants (Petrie et al., 2002; Wang et al., 2006; Li et al., 2008). However, most of these results were mainly derived from the laboratory experiments. Therefore, under the natural conditions, further investigations are still needed to determine the role of iron and manganese oxide in transformation of chlorinated organic pollutants. Finally, soil is generally considered as an important sink of persistent organic pollutants in the environment. However, soil with large quantities of accumulated pesticide may have been an important re-emission source attributable to the redistributions of pesticide in the environment after the termination of application of these compounds (Tao et al., 2008). Therefore, the re-emission of HCHs and DDTs from contaminated soil is another important fate process and investigating the factors affecting the re-emission potential of OCPs in soil under the natural conditions is also very important.

The PRD (Fig. 1), as one of the most economically prosperous regions in China, has been well developed agriculturally and consumed the highest amount of pesticides per unit (37.2 kg/ha) of agricultural land in the country (Zhang et al., 2002). As a result, numerous studies on OCPs in this area have been conducted (Zhang et al., 2002; Wang et al., 2007; Guo et al., 2008; Guan et al., 2009; Ma and Ran, 2009). However, these studies rarely focused on the potential influence factors such as soil properties and land use types on the environmental fate of OCPs. Therefore, the objective of the present study was to examine the impact of soil physiochemical properties on the distribution patterns and fate of soil HCHs and DDTs on a large spatial scale. To accomplish this objective, in addition to the measurement of HCHs and DDTs in soil from different land use types and soil textures throughout the entire PRD, selected physiochemical parameters including pH, TOC, total Fe (TFe), DCB-Fe (DFe), amorphous-Fe (AFe), complexed-Fe (CFe), total Mn (TMn), DCB-Mn (DMn), amorphous-Mn (AMn), complexed-Mn (CMn), and cation exchange capacity (CEC) were also determined. In addition, potential ecological risk posed by soil HCHs and DDTs were also assessed.

## 2. Materials and methods

### 2.1. Materials

The mixed standard solutions of 1000 µg/ml including *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, and  $\delta$ -HCH were all obtained from Ultra Scientific (North Kingston, RI, USA). Neutral silica gel (80–100 mesh, reagent grade, Branch of Qingdao Haiyang Chemical Company, Qingdao, China) and alumina (100–200 mesh, reagent grade, Shanghai five four chemical reagent company, Shanghai, China) were purified with methanol for 48 h and then exchanged the solvent as dichloromethane (DCM) for another 48 h with a Soxhlet extractor. Upon drying at room temperature, silica gel and alumina were baked at 180 °C and 250 °C, respectively, for 12 h. Sodium sulfate (analytical grade, Guangzhou chemical reagent factory, Guangzhou, China) was baked at 450 °C and stored in sealed containers. Methanol and *n*-hexane (Fisher Scientific International, Hampton, VA, USA) were both of high performance liquid chromatograph grade and used as supplied.

### 2.2. Sample collection and extraction

A total of 151 soil samples were collected between October and December 2006 from nine cities in the PRD (Fig. 1), with 27 from

Dongguan (five for fruit, three for paddy and 19 for vegetable), 11 from Foshan (one for fruit, two for forest, five for paddy and three for vegetable), 16 from Guangzhou (five for fruit, two for forest, four for paddy and five for vegetable), 27 from Huizhou (one for fruit, eight for paddy and 18 for vegetable), nine from Jiangmen (two for forest and seven for paddy), six from Shenzhen (two for fruit, three for forest and one for vegetable), 26 from Zhuhai (14 for fruit, six for paddy and six for vegetable), five from Zhaoqing (one for forest and four for paddy), and 24 from Zhongshan (six for fruit, eight for paddy and 10 for vegetable). Upon return to the laboratory, the soil samples were freeze-dried, ground into powders, sieved to <2 mm, and stored in glass bottles prior to extraction.

A detailed description of the analytical procedure was given elsewhere (Boul, 1996; Gong et al., 2004; Vagi et al., 2007). Briefly, each soil sample (~20 g dry weight) wrapped with a filter paper cleaned with methanol and DCM was placed in a 250 ml Soxhlet extractor. After spiking with 2 g of activated Cu mesh for desulfurization and surrogate standard 4, 4'-dichlorobiphenyl (PCB 15), the samples were Soxhlet extracted with DCM for 48 h. The extract was concentrated, solvent-exchanged to hexane, and further purified on a glass column packed with alumina/silica in 1:2 volume ratio. The target compounds were eluted with 70 ml of a mixture of DCM and *n*-hexane (3:7 in volume). The eluted solvent was then vacuum-evaporated to approximately 1 ml and concentrated to 0.2 ml under a gentle nitrogen flow.

### 2.3. Instrument analysis

The concentrations of the target compounds were measured with a Shimadzu gas chromatograph (GC) 2010 equipped with a <sup>63</sup>Ni electron capture detector (ECD) and a DB-5 silica fused capillary column (30 m long × 0.32 mm i.d. × 0.25 µm film thickness). Nitrogen (99.999% in purity) was used as the carrier and make-up gas at 2.5 ml/min. The injector and detector temperatures were 260 and 310 °C, respectively. The gas chromatographic column temperature was initially set at 100 °C for 6 s, ramped at 4 °C/min to 290 °C, and then held at 290 °C for 10 min. Quantification was performed using an internal calibration method based on five-point calibration concentration levels for individual components. Decachlorobiphenyl was used as the internal standard for GC-ECD quantitative analyses. In addition, a standard solution of *p,p'*-DDT was analyzed once for every batch of 10 samples prior to instrumental analysis to ensure the degradation rate of *p,p'*-DDT in the inject port was less than 20% during instrumental analysis.

### 2.4. Quality control and quality assurance

The detection limits ranged from 0.005 to 0.02 µg/kg, estimated by three times the signal to noise ratio. The recoveries of the surrogate standard PCB 15 in all samples were in the range of 81–110%. Three blank samples undergoing the entire analytical procedure were analyzed to assess possible interferences from the reagents and glassware. Because the concentrations in the procedural and field blank samples were close to or lower than the detection limits, they were not subtracted out for all the samples.

### 2.5. Measurements of soil physiochemical properties

To measure soil pH, 10 g of air-dried soil previously passed through a 60 mesh sieve was suspended in 25 ml deionized water, shaken for 1 h, then decanted after settling for 30 min. Then, a potentiometric glass electrode was placed into the soil suspension to obtain pH value once the reading became stabilized (Pansu and Gautheyrou, 2006). Total organic carbon was measured with a CNS-analyzer (Elementar Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany). Particle-size distribution was determined with a pipette method (Pansu and Gautheyrou, 2006), while soil texture was classified based on a

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