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Sources and transformation pathways for dichlorodiphenyltrichloroethane (DDT) and metabolites in soils from Northwest Fujian, China☆

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ABSTRACT

Dicofol (2,2,2-trichloro-1,1-bis-(*p*-chlorophenyl)ethanol) found in the environment is not only a miticide originated from commercial use, but also a metabolite of dichlorodiphenyltrichloroethane (DDT), which is often overlooked. To verify the sources and transformation pathways of DDT and related metabolites in soils, we measured *p,p'*-(dicofol + DBP) (sum of *p,p'*-dicofol and 4,4′-dichlorobenzophenone), DDT and six metabolites in soils from Northwest Fujian, China. The ratios of 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*o,p'*-DDT)/1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDT) and the mass balance demonstrated that *p,p'*-(dicofol + DBP) predominantly originated from *p,p'*-DDT transformation rather than from actual dicofol application. *p,p'*-(dicofol + DBP) accounted for 45.0% as the primary metabolites of DDT in this study, more than 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (*p,p'*-DDE) and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDD), which might lead to large overestimations of the fresh DDT input by using the traditional ratio of $(\sum_2 DDD + \sum_2 DDE)/\sum_2 DDT$ (with all *o,p'*- and *p,p'*- isomers included). In paddy fields where the conditions alternate between aerobic (dry period) and anaerobic (wet period), both *p,p'*-DDD and *p,p'*-DDE were likely to degrade to 1-chloro-2,2-bis-(*p*-chlorophenyl)ethylene (*p,p'*-DDMU), which further transformed to 2,2-bis(*p*-chlorophenyl) ethylene (*p,p'*-DDNU). Degradation of *p,p'*-DDMU to *p,p'*-DDNU mainly occurred in waterlogged paddy soils. However, *p,p'*-DDNU might not transform to other higher-order metabolites in aerobic surface soils. Overall, our study confirmed *p,p'*-(dicofol + DBP) as metabolites of *p,p'*-DDT, suggested DDE and DDD were parallel precursors of DDMU, and further verified the transformation pathways of DDT in surface soils.

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1. Introduction

Dicofol (2,2,2-trichloro-1,1-bis-(*p*-chlorophenyl)ethanol) is one of the major organochlorine acaricides widely used in controlling mites after DDT was banned in 1983 in China, due to its broad spectrum of activity, effectivity, and low-cost (Luo et al., 2014). Commercial dicofol (c-dicofol) in China contains 11.4%, 6.9%, 4.4%, and 1.7% of 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane (*o,p'*-DDT), intermediate 2,2,2-trichloro-1,1-bis-(*p*-chlorophenyl)-1-chloroethane (α-chloro-DDT), 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (*o,p'*-DDE), and 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDT) on average, respectively, resulting in serious DDT pollution (Purnomo et al., 2008). Moreover, dicofol may also originate from DDT transformation by the fungus *Phanerochaete chrysosporium* in the following pathway: *p,p'*-DDT → *p,p'*-dicofol → 2,2-dichloro-1,1-

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bis(*p*-chlorophenyl)ethanol (FW-152) → 4,4′-dichlorobenzophenone (*p,p'*-DBP) (Bumpus and Aust, 1987). The pathway of [^{14}C] *p,p'*-DDT → [^{14}C] *p,p'*-dicofol was proved to be controlled by the lignin degrading system (Bumpus and Aust, 1987), as mineralization and dicofol production were observed only after ligninase was established, which was also presented by Aislabie et al. (1997). However, most studies took dicofol as a major source of DDT for granted (Qiu et al., 2005; Yang et al., 2008; Li et al., 2015) with few efforts made on this DDT degradation pathway involving *p,p'*-dicofol in the environment.

Except for the above degradation pathway, DDT can degrade to diverse metabolites before eventually being mineralized (Wedemeyer, 1967; Quensen et al., 1998; Mwangi et al., 2010). Sudharshan et al. (2012) reviewed the decomposition of DDT through anaerobic degradation by reductive dechlorination, and biodegradations by single or combination of microbial species in pathways of *p,p'*-DDT → 1,1-dichloro-2,2-bis-(*p*-chlorophenyl) ethane (*p,p'*-DDD) → 1-chloro-2,2-bis-(*p*-chlorophenyl)ethylene (*p,p'*-DDMU) → 1-chloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p'*-DDMS) → 2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDNS), and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (*p,p'*-DDE) → *p,p'*-DDMU → 2,2-bis(*p*-chlorophenyl)ethylene (*p,p'*-DDNU). When subjected to aerobic biotic degradation, abiotic dehydrochlorination and photochemical degradation, the decomposition was accompanied with the formation of DDE, though DDE was not deemed to degrade under aerobic conditions (Aislabie et al., 1997).

Notably, all the studies discussed above were carried out under lab-controlled conditions, usually in minimal media or marine sediments. However, the degradation processes in complex heterogeneous matrices, e.g. soil, are different and much slower. Many soil parameters, such as temperature (Guenzi and Beard, 1976; Eggen and Majcherczyk, 2006), pH (Purnomo et al., 2008), organic matter (Aislabie et al., 1997), and biotic populations, including microorganism (Hay and Focht, 2000; Megharaj et al., 2000), fungi (Purnomo et al., 2010; Xiao et al., 2011), and invertebrates, such as earthworms (Lin et al., 2012), would strongly affect the DDT transformation routes and rates. The half-life of DDT in soils might vary from 3 to 30 years under natural conditions (Lin et al., 2012). Eganhouse and Pontolillo (2008) also indicated that the *in-situ* rate of DDE transformation was 2–4 times slower than that determined in laboratory microcosm experiments. DDT and related metabolites can be uptaken by plants (Lunney et al., 2004) which tend to accumulate in primary products and pass on to the predators to store in the fatty tissues of organisms through the food chain (Aislabie et al., 1997; Naso et al., 2003). Some higher order metabolites are also water soluble, suggesting a higher bioavailability (Semple et al., 2004) than parent DDT and primary metabolites in soils. For example, the water solubility of 2,2-bis(4-chlorophenyl) acetic acid (*p,p'*-DDA) and *p,p'*-DBP at 25 °C are 5.85 and 3.80 mg/L (estimated by EPIWEB 4.1), respectively, which are much higher than that of *p,p'*-DDT (7.30×10^{-3} mg/L) and *p,p'*-DDE (2.65×10^{-2} mg/L). Although the acute assessment of every DDT metabolite on human health is not available, the possibility of chronic effects (Aislabie et al., 1997), cytotoxic and estrogenic activities (Wetterauer et al., 2012) cannot be ruled out. However, only a few studies have been conducted on DDT metabolites in natural environments worldwide. Among them, most studies focused on water and marine sediment (Quensen et al., 1998; Guo et al., 2009; Yu et al., 2011). Soil is one of the largest reservoirs of organochlorine pesticides (OCPs) in the terrestrial environment (Wang et al., 2006; Yuan et al., 2014). A lot of field investigations in soils just stopped at the pathways of DDT → DDE and DDT → DDD, which were thought to be the dominant pathways (Jiang et al., 2009). However, that may not be the real case now. After decades of use and aging, more and more metabolites appear and become abundant. Thus, further study of degradation of DDT and its metabolites in soils, especially under field conditions, is necessary for better understanding of the degradation pathways of DDT.

Fujian Province with a total area of 12.4×10^4 km^2, located in the southeast of China (Fig. 1), was one of the four largest DDT consumer provinces from 1950s to 1980s (the other three provinces were Zhejiang, Shanghai, and Guangdong) in China (Wang et al., 2005). Northwest Fujian (116.02°–120.24° E and 24.68°–29.87° N), including the cities of Longyan, Sanming, Nanping, and Ningde, accounts for 2/3 of the area of Fujian and is referred as the "Granary of Fujian". This area has a subtropical climate with annual average temperatures of 17–21 °C, and annual average rainfall of 1400–2000 mm. Red soil and yellow soil with high organic matter are dominant (Qu et al., 2015a). The climate, characterized by strong solar radiation, high annual accumulated temperature, humidity and abundant rainfall, favors the degradation of DDT in soils. In this study, the contents of *p,p'*-dicofol, *p,p'*-DBP, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*o,p'*-DDD), *p,p'*-DDMU, and *p,p'*-DDNU, (sum of them is presented as $\sum_{10}$DDT), were investigated in surface soils of Northwest Fujian to: 1) diagnose the sources of *p,p'*-(dicofol + DBP); 2) quantify the influence of metabolites on the DDT source diagnose in natural environment; and 3) verify the relevant possible transformation pathways of DDT in surface soils.

2. Methods

2.1. Sample collection

In March 2009, surface soil samples (0–20 cm) were collected from 135 gridding squares covering the whole Northwest Fujian (Fig. 1). At each square (24 × 24 km), a representative sample of native soil (ca. 1 kg) was obtained by combining the five-homogenized sub-samples: one from the central site and four sub-soils collected from four directions within a circle of radius 100 m, using a pre-cleaned stainless-steel scoop. Each soil sample was wrapped in aluminum foil (to prevent the soil in direct contact with the polythene bag), and packed into a sealed polythene bag. Samples were defined as paddy (n = 83) or non-paddy soils (n = 52) according to the collection geography. All samples were

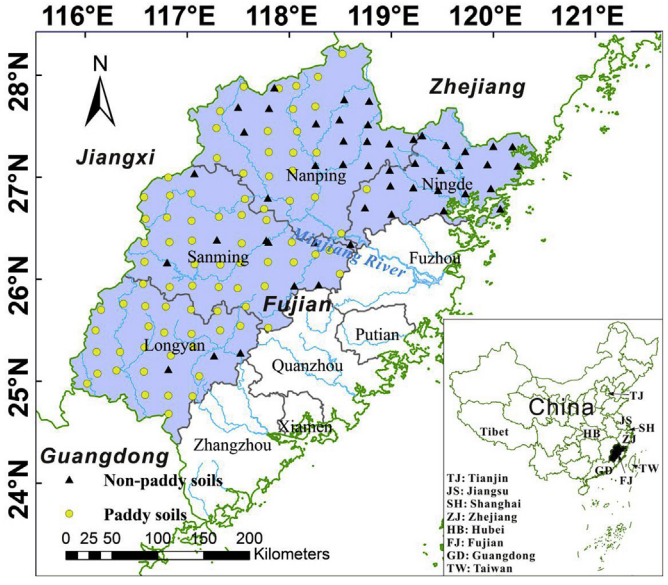

Fig. 1. Sampling sites for soils in Northwest Fujian, China.

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