Concentrations of DDTs and Enantiomeric Fractions of Chiral DDTs in Agricultural Soils from Zhejiang Province, China, and Correlations with Total Organic Carbon and pH

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Ⓢ *Supporting Information*

ABSTRACT: Dichlorodiphenyltrichloroethanes (DDTs) are persistent organic pollutants that were widely used in China, especially eastern China, as insecticides. This work investigated the concentration, dissipation, and volatilization of DDTs and enantiomeric fractions (EFs) of o,p'-DDD and o,p'-DDT in agricultural soils collected in 2006 from 58 sites in Zhejiang province. Correlations between DDT residues and soil properties were assessed to determine the effect of soil properties on the environmental attenuation of DDTs. High concentrations and detection frequencies were found for DDTs in agricultural soils in the region even though large-scale use of DDTs was banned over 20 years ago. The amount of DDTs was about 485 tons in the upper 20 cm of the soil column of cropland in the province in 2010, with a dissipation half-life of ∼9 years. The mass flux of DDTs was 43 ng m^{-2} h^{-1}, which corresponds to emissions of 7.6 tons with an emission factor of 1.6% in 2006. The low p,p'-DDT/p,p'-DDE ratios and high o,p'-DDT/p,p'-DDT ratios suggest that there were no recent inputs of DDTs but fresh application of dicofol, which contains DDT (o,p'-DDT in particular) impurities. The significant positive correlation between concentrations of DDTs and total organic carbon content (TOC) indicates the distribution of DDTs fit a typical "secondary distribution" pattern. DEVrac of o,p'-DDD, which is defined as the absolute value of EFs subtracted from 0.5, was significantly related with most of the physicochemical and microbial soil properties. The most significant correlation is that between DEVrac of o,p'-DDD and soil pH ($p < 0.001$), indicating that the soil pH plays a key role in enantioselective residues of DDTs.

KEYWORDS: *soil, DDTs, dissipation, volatilization, enantiomeric fraction*

■ INTRODUCTION

Dichlorodiphenyltrichloroethanes (DDTs), the sum of DDT-related compounds (p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p, p'-DDD, and o,p'-DDD), are persistent organic pollutants (POPs) restricted or banned in many countries under the Stockholm Convention.[1] DDTs have been studied extensively in the past 30 years, revealing the exposure of wildlife and humans to DDTs[2−6] and the degradation, distribution, and potential for long-range transport of these chemicals.[7−13] However, this kind of research on DDTs has been rarely conducted in environmentally sensitive regions, such as developing countries, due to lack of financial and technological support. Furthermore, these countries have banned or restricted the use of DDTs relatively recently.

China was a major producer and consumer of DDTs from 1952 until 1984 when their use was banned on crops. Over this period, the total Chinese production of DDTs (0.4 million ton) accounted for 20% of the total production in the world.[14] Zhejiang province in eastern China had one of the highest application records of DDTs in China.[15−17] It is estimated that the total consumption of DDTs in Zhejiang was over 30000 tons from 1952 to 1984 and accounted for about $^{1}/_{10}$ of the national application.[18] As a result, high levels of DDT residues have been found in food and human tissues in the region.[19] Therefore, it is important to assess residues of DDTs in this province, and such studies may be useful in elucidating the distribution, dissipation, and volatilization of DDTs in the region.

The distribution of DDTs in soil has been a common subject of investigations, which provided pictures of DDT contamination across the world.[20−25] In contrast to distribution, which indicates residue levels of pollutants at a specific time, dissipation is a dynamic process that can be used to examine the possible trend of contamination. The previous studies on dissipation of DDTs were mainly conducted under laboratory conditions and at specific sites in soil.[26,27] The dissipation of DDTs in large-scale field studies is very limited because of the lack of usage data and temporal residues of DDTs in soil. The usage inventory of DDTs in soil in Zhejiang has been

developed, and determination of dissipation of DDTs is therefore practical by comparing usage inventory with residues. The results can give insight on the persistence of DDTs in agricultural soil in Zhejiang. Volatilization of DDTs from soils and the distribution and dissipation of DDTs in soil are environmental issues of long-term public concern.[28] Several studies have evaluated the volatilization half-life and emission amount of DDTs in soils.[28,29] For example, research in the southern United States indicated that the volatilization half-life of *p,p'*-DDE ranged from 11 years for tilled soil to 63 years for untilled soil.[29] A much higher volatilization half-life of 220 years for DDTs was observed for the largest vegetable farming area in southern Ontario, Canada.[28] The results in these studies provided the references for estimating volatilization of DDTs from soils to the atmosphere in Zhejiang, China.

Two chemicals among DDTs, *o,p'*-DDT and *o,p'*-DDD, are chiral and undergo degradation at different rates in soil. Physicochemical and microbial soil properties were thought to be responsible for fluctuation of enantiomeric fractions (EFs) of chiral DDTs in soils by influencing the activity of the microbial community,[30] and they also have a profound impact on the residues level of DDTs.[28] Kurt-Karakus used linear correlation to analyze the relationship between DEVrac of chlordane (defined as the absolute value of EFs subtracted from 0.5) and soil properties and found a significant positive correlation between DEVrac and soil organic matter (SOM).[20] Our previous study indicated that the distribution of hexachlorocyclohexanes (HCHs) in agricultural soil in Zhejiang was predominately influenced by soil temperature.[31] In addition, it has been shown that the correlation of the DDT concentrations and EFs of chiral DDTs with the soil properties can be used to identify key factors which control the distribution pattern and enantioselective degradation of DDTs.[20]

The present work reports the residues of DDTs in soil collected at 58 locations in Zhejiang, China. The specific objectives of this study include (i) investigating the spatial distribution, dissipation, and volatilization of DDTs in Zhejiang province, (ii) examining the EFs and enantioselective degradation of *o,p'*-DDD and *o,p'*-DDT in the agricultural soils, and (iii) identifying the key soil properties that control the distribution pattern and enantioselective degradation of DDTs.

■ EXPERIMENTAL PROCEDURES

Chemicals. Standards of DDTs were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. Solvents including dichloromethane (DCM), hexane, and isooctane were purchased from TEDIA (HPLC or glass-distilled grade, Shanghai, China). Silica and aluminum were purchased from Merck Chemicals (Shanghai, China). Anhydrous granular sodium sulfate was obtained from Hangzhou Huipu Co. Ltd., China, and baked at 400 °C overnight before use.

Sample Collection Extraction and Analysis. Fifty-eight surface agricultural soil samples (at a depth of 20 cm) were collected by hand-held coring device in 2006, as described in our previous studies.[31,32] Details of the sampling and soil parameters that were determined according to the methods in our previous studies[31,32] are presented in Table SI-1 in the Supporting Information.

Prior to extraction of DDT residues, the soil samples were homogenized using a mortar and pestle until a granular consistency was achieved. An aliquot of the soil sample was spiked with surrogate standard of decachlorobiphenyl (PCB209) and extracted in a Soxhlet apparatus for 20 h using DCM. A method blank was run with every sample batch (*n* = 8) using 15 g of sodium sulfate to check for potential contamination. The extracts were cleaned up by online gel permeation chromatography (GPC) and a concentration and evaporation process system using a column packed with Bio-Beads S-X3 (2.5 cm (i.d.) × 40 cm, 200−400 mesh) (GPC Ultra 10836, LCTech GmbH, Munich, Germany). Subsequently, the extracts were concentrated to 1−2 mL by gentle nitrogen blow-down using iso-octane as a keeper for the extracts. The iso-octane extracts were further cleaned using 4 g of 3% deactivated silica gel column topped with 2 g of 6% deactivated aluminum. After preconditioning with 10 mL of 5:95 (v/v) DCM/hexane, the column was loaded with the sample and then finally eluted with 15 mL of hexane and 70 mL of 30:70 (v/v) DCM/hexane. The first 10 mL of hexane elution was discarded to minimize interferences with polychlorinated biphenyl (PCB) congeners and nonpolar compounds. The remaining effluent was concentrated to 5 mL by gentle nitrogen blow-down using iso-octane as a final solvent for the extracts. Ultimately, the sample was further cleaned up by shaking with 0.5 mL of 18 M sulfuric acid. Prior to injection, the injection standard pentachloronitrobenzene (PCNB) was added for volume correction.

Analysis of the samples was performed using gas chromatography (Agilent 6890 GC-ECD). Aliquots of 1 μL were injected on a Zebron MultiResidue-1 column (30 m, 0.25 mm i.d., 0.25 μm film; Phenomenex Inc.) and an HP-5 column for confirmation (30 m, 0.25 mm i.d., 0.25 μm film; Agilent Technologies Inc.) by 7683B autosampling. Helium was used as the carrier gas, and the flow rate was constant at 3.4 mL min⁻¹. The injector temperature was held constant at 250 °C. The temperature program for the Zebron MultiResidue-1 column was as follows: initial temperature, 100 °C (hold for 0.5 min); increased at 35 °C min⁻¹ to 220 °C; and finally increased at 20 °C min⁻¹ to 280 °C (hold for 10 min). The oven program for the HP-5 column was as follows: initial temperature, 80 °C (hold for 1 min); increased at 10 °C min⁻¹ to 200 °C; increased at 1 °C min⁻¹ to 225 °C (hold for 1 min); and finally increased at 15 °C min⁻¹ to 260 °C (hold for 5 min).

Enantiomer analysis was performed using gas chromatography−negative ion mass spectrometry (Agilent 7890 GC-5973MSD). Aliquots of 1 μL were injected on a BGB-172 column (20% *tert*-butyldimethylsilylated *β*-cyclodextrin in OV-1701, 30 m, 0.25 mm i.d., 0.25 μm film; BGB Analytik AG) by 7683B autosampling. The temperatures of the ion source and quadrupole were set at 150 °C. Helium was used as the carrier gas, and the flow rate was constant at 1 mL min⁻¹. The flow rate of reagent gas (methane) was set at 40%. The injector temperature was held constant at 250 °C. The temperature of the GC was held constant at 90 °C for 1 min, increased at 15 °C min⁻¹ to 160 °C, increased at 1 °C min⁻¹ to 190 °C (hold for 35 min), and finally increased at 20 °C min⁻¹ to 230 °C (hold for 20 min). The target/qualifier ions were *m/z* 246 and 248 for both *o,p'*-DDD and *o,p'*-DDT.[20] The ions *m/z* 235 and 237 were not used because of their higher background compared to *m/z* 246 and 248. The elution order of *o,p'*-DDD and *o,p'*-DDT enantiomers was determined by enantiopure standards collected from the outlet of a chiral JASCO LC-2000 series high-performance liquid chromatography (HPLC) system (JASCO, Tokyo, Japan) as described by Yuan et al.[21] The (+)-enantiomer first eluted for *o,p'*-DDD, whereas the (−)-enantiomer first eluted for *o,p'*-DDT, in the BGB-172 column.

Calculation of Dissipation Half-Life and Volatilization of DDTs in Soil. The following equations are widely used to evaluate dissipation of DDTs in soil.[27]

$$C_{DDTs}(t) = C_{DDTs}(0) \exp(-k_d t) \tag{1}$$

$$t_{d1/2} = 0.693/k_d \tag{2}$$

k_d is the first-order dissipation rate constant, $t_{d1/2}$ is the dissipation half-life, $C_{DDTs}(0)$ is the concentration in the starting year, and $C_{DDTs}(t)$ is the concentration in the monitoring year t (i.e., 2006). The starting year is assumed to be 1968 (the median between 1952 when the DDTs started to be used and 1984 when the large-scale use of DDTs was stopped).

To evaluate the dissipation half-life of DDTs in the province, we calculated the mean usage concentrations of DDTs over the 58 sampling sites by using the data sets from gridded DDT usage

Table 1. Detectable Frequency, Geometric Mean, Arithmetic Mean, Median, and Concentration Range of DDT Components

compound	detectable frequency (%)	arithmetic mean ± SD (ng g^{-1} dw)	geometric mean (ng g^{-1} dw)	median value (ng g^{-1} dw)	min (ng g^{-1} dw)	max (ng g^{-1} dw)
p p′-DDE	100	21 ± 23	7.0	5.4	0.83	199
p,p′-DDD	97	20 ± 25	3.7	1.9	BDL^a	451
p,p′- DDT	81	9.6 ± 11	2.2	3.0	BDL	128
o,p′-DDD	86	10 ± 13	1.5	1.4	BDL	92
o,p′-DDT	81	21 ± 29	2.8	2.1	BDL	283
ΣDDTs	100	82 ± 86	31	23	4.0	529

^{a}BDL, below detection limit.

inventories from 1952 to 1984 developed by Li and co-workers[18] (see Figure SI-1, Supporting Information). The mean usage concentration of DDTs is estimated to be 1500 ng g^{-1}.

The mass flux (dM_{DDT}/dt) of DDTs (i.e., volatilization amount of DDTs from soil to air) was calculated using the equation[28]

$$dM_{DDT}/dt = -k_v M_{DDT} \qquad (3)$$

where M_{DDT} is the mass of DDTs in a block soil of 1 m^2 × 0.05 m thick, density = 1460 kg m^{-3}, and k_v is the first-order volatilization rate constant.

Previously, k_v values of 7.19 × 10^{-6} h^{-1} from the southern United States[33] and 5.37 × 10^{-7} h^{-1} from southern Ontario, Canada,[28] have been reported. In this work, the former was adopted because the two key parameters influencing the residues of DDTs in soil (i.e., soil total organic carbon (TOC) and temperature) were similar between our study in Zhejiang, China, and the southern United States.[29] The ranges of soil TOC were 0.13−3.01 and 0.47−2.39% in Zhejiang (Supporting Information Table SI-1) and in the southern United States, respectively,[29,32] and the ranges of annual temperature were 10−20 and 13−24 °C for Zhejiang[31] and the southern United States, respectively (http://www.srcc.lsu.edu/climateNormals/). In contrast, different TOC values (i.e., 42%)[28] and annual temperatures (i.e., 2−12 °C) (http://visitguelphwellington.ca/Modules/Pages/Default.aspx?ID=18&MenuID=49) were measured in southern Ontario, Canada.

Quality Assurance/Quality Control. The limit of detection (LOD) was defined as the average blank level plus 3 times the standard deviation. The LOD values were 0.05 ng g^{-1} dry weight (dw) for p,p′-DDE, 0.10 ng g^{-1} dw for p,p′-DDD and p,p′-DDT, 0.03 ng g^{-1} dw for o,p′-DDD, and 0.30 ng g^{-1} dw for o, p′-DDT. Recoveries were routinely monitored in every sample using the surrogate standard of PCB209. The mean recoveries were 78 ± 9% for PCB209, indicating a small proportion of PCB209 was lost during the extraction and cleanup process. However, the recoveries were similar to those previously reported.[22] An additional matrix spiked recovery test was performed by spiking a DDT mixture to soils in which DDT residues were close to or below the detection limits. After correction for the concentration of DDTs in the soil, recoveries ranged from 77 to 118%.

Results of chiral analysis were expressed as the EF, which is defined as the ratio of peak area of the (+)-enantiomer to the sum peak area of the (+)- and (−)-enantiomers.[20] The EF values must meet the following criteria: (i) differences in area ratios of the two monitored ions must be within ±0.05 between the sample and standard, and (ii) differences in EF values must be within ±0.05 between the two monitored ions.[25] Replicate injections of racemic standards, which were made for every five samples, were 0.502 ± 0.003 for o,p′-DDD and 0.496 ± 0.005 for o,p′-DDT. Average EFs and standard deviations for the soils were calculated from replicate injections of separately extracted portions of the soil.

Statistical Analyses. Statistical analyses were performed using Origin (version 8.0, OriginLab Data Analysis and Graphing Software, Guangzhou, China) for Windows (version 8) and Microsoft Excel at a significance level of α = 0.05. All data were normally distributed as determined by the Kolmogorov−Smirnov test. Linear correlation analysis employed in Kurt−Karakus's work[20] was used for all correlations, and the significance (p value) was analyzed by the Fisher's F test. The Student t test was used to justify the significant

difference of EFs between samples and standards.[34] Any measured samples reported lower than the LOD were calculated to be 0.5 of the LOD for statistical analysis as recommended by the U.S. Environmental Protection Agency.[35]

■ RESULTS AND DISCUSSION

DDTs Residues in Soils. The detailed DDT residues in 58 samples are shown in Table SI-2 and Figure SI-2 in the Supporting Information. Table 1 shows levels for DDTs (total DDTs) ranging from 4.0 to 530 ng g^{-1} dw with a geometric mean (GM) of 31 ng g^{-1} dw and an arithmetic mean of 82 ± 86 ng g^{-1} dw. The large standard deviation of the arithmetic means indicates that the concentrations of DDTs vary from location to location in the province. As shown in Figure.1, most
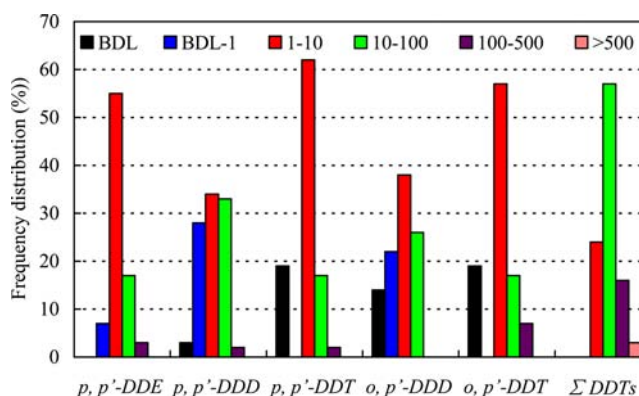
Figure 1. Frequency distribution for concentration of five DDT components and DDTs (concentration unit, ng g^{-1} dw).

of the soil samples had levels of DDTs ranging from 10 to 100 ng g^{-1} dw (57% of the samples), followed by 1−10 ng g^{-1} dw (24%), 100−500 ng g^{-1} dw (16%), and >500 ng g^{-1} dw (3%). Among DDTs analyzed, p,p′-DDE was the predominant compound (geometric mean of 7.0 ng g^{-1} dw and arithmetic mean of 21 ng g^{-1} dw), followed by p,p′-DDD (geometric mean of 3.7 ng g^{-1} dw and arithmetic mean of 20 ng g^{-1} dw). Concentrations of o,p′-DDD and o,p′-DDT were above the detection limit in ∼86 and ∼81% of the samples, respectively. p,p′-DDT was detected in ∼81% of the agricultural soil samples. A comparison between the concentration of residues and usage concentrations that were calculated by using the data sets from gridded DDT usage inventories from 1952 to 1984 developed by Li and co-workers[18] shows no significant correlation between residues and usage at the 58 sampling sites. The residue levels of DDTs in agricultural soils in Zhejiang were similar to those reported in the Pearl River Delta (median value of 20−25 ng g^{-1}),[22] Tianjin (average of 80 ng g^{-1}),[23] and Haihe plain (average of 63.6 ng g^{-1})[24] in China, but higher than those in agricultural soils from the U.S. Corn

Table 2. Enantiomeric Fractions of o,p'-DDD and o,p'-DDT

sample	o,p'-DDD	o,p'-DDT	sample	o,p'-DDD	o,p'-DDT
HZ 1	0.569 ± 0.014[a]	0.414 ± 0.031[b]	JH 1	0.451 ± 0.020[b]	0.514 ± 0.020[c]
HZ 2	0.440 ± 0.012[b]	0.677 ± 0.019[a]	JH 2	0.383 ± 0.013[b]	NA
HZ 3	NA	0.426 ± 0.008[b]	JH 3	NA	0.725 ± 0.022[a]
HZ 4	NA	0.586 ± 0.020[a]	JH 4	0.554 ± 0.024[a]	0.371 ± 0.015[b]
HZ 5	NA	0.265 ± 0.011[b]	JH 5	0.231 ± 0.005[b]	0.362 ± 0.012[b]
HZ 6	0.564 ± 0.018[a]	0.544 ± 0.032[a]	SX 1	0.444 ± 0.013[b]	0.505 ± 0.021[c]
HZ 7	0.396 ± 0.011[b]	0.383 ± 0.005[b]	SX 2	0.428 ± 0.017[b]	0.339 ± 0.014[b]
HZ 8	0.573 ± 0.009[a]	0.458 ± 0.012[b]	SX 3	0.592 ± 0.021[a]	0.670 ± 0.010[a]
HZ 9	0.378 ± 0.012[b]	0.469 ± 0.023[b]	SX 4	0.568 ± 0.024[a]	NA
HZ 10	0.515 ± 0.013[a]	0.534 ± 0.005[a]	SX 5	0.132 ± 0.006[b]	0.438 ± 0.012[b]
HZ 11	0.216 ± 0.012[b]	0.482 ± 0.011[b]	QZ 1	0.183 ± 0.014[b]	0.499 ± 0.023[c]
HZ 12	0.372 ± 0.016[b]	0.514 ± 0.020[c]	QZ 2	0.462 ± 0.021[b]	NA
JX 1	0.430 ± 0.015[b]	0.640 ± 0.009[a]	WZ 1	0.352 ± 0.014[b]	0.461 ± 0.015[b]
JX 2	0.375 ± 0.016[b]	0.685 ± 0.017[a]	WZ 2	0.607 ± 0.017[a]	NA
JX 3	0.362 ± 0.012[b]	0.485 ± 0.012[b]	WZ 3	0.094 ± 0.005[b]	0.498 ± 0.015[c]
JX 4	NA	NA	NB 1	0.455 ± 0.013[b]	0.789 ± 0.023[a]
JX 5	0.593 ± 0.030[a]	NA	NB 2	0.451 ± 0.016[b]	0.892 ± 0.014[a]
JX 6	0.610 ± 0.022[a]	0.437 ± 0.011[b]	NB 3	0.558 ± 0.023[a]	NA
JX 7	0.554 ± 0.024[a]	0.175 ± 0.016[b]	NB 4	0.410 ± 0.021[b]	NA
JX 8	0.580 ± 0.019[a]	0.501 ± 0.017[c]	NB 5	0.280 ± 0.007[b]	0.452 ± 0.015[b]
JX 9	0.475 ± 0.011[b]	0.487 ± 0.004[b]	TZ 1	NA	0.432 ± 0.014[b]
JX 10	NA	0.239 ± 0.013[b]	TZ 2	NA	NA
JX 11	0.635 ± 0.009[a]	0.486 ± 0.013[b]	TZ 3	0.405 ± 0.015[b]	0.710 ± 0.024[a]
HUZ 1	NA	0.653 ± 0.027[a]	TZ 4	0.070 ± 0.005[b]	0.510 ± 0.019[c]
HUZ 2	NA	NA	ZS 1	0.395 ± 0.013[b]	NA
HUZ 3	0.563 ± 0.015[a]	0.634 ± 0.029[a]	ZS 2	0.056 ± 0.003[b]	0.453 ± 0.024[b]
HUZ 4	NA	NA	LS 1	0.537 ± 0.009[a]	0.639 ± 0.014[a]
HUZ 5	0.437 ± 0.012[b]	0.427 ± 0.007[b]	LS 2	0.525 ± 0.018[a]	0.506 ± 0.010[c]
HUZ 6	0.543 ± 0.021[a]	0.681 ± 0.019[a]			
HUZ 7	0.391 ± 0.008[b]	0.490 ± 0.011[c]			

[a]EF > racemic. [b]EF < racemic. [c]EF is not significantly different from racemic (t test).

Belt (geometric mean of 9.63 ng g^{-1})[25] and lower than those in agricultural soils from southern Ontario, Canada (19000 ng g^{-1}).[28] The results indicate that a potential risk to the environment exists in the region even more than 20 years after DDTs were banned in large scale.

Dissipation of DDTs in Soils. Equation 1 results in a k_d of 0.076 year^{-1} with $C_{DDTs}(0) = 1500$ ng g^{-1} and $C_{DDTs}(t = 38) = 82$ ng g^{-1} dw. The half-life ($0.693/k_d$) was calculated to be ~9 years. It is interesting to note that this dissipation half-life is similar to the volatilization half-life for tilled soil in the southern United States (i.e., 11 years),[29] but much smaller that the volatilization half-life for historically treated soil in southern Ontario, Canada (i.e., 220 years).[28] This implies that DDTs would more easily dissipate in soil with high temperature and low TOC than in soil with low temperature and high TOC. The global distribution of DDTs might be high in areas with low temperature and high TOC but low in areas with high temperature and low TOC.

Volatilization of DDTs from Soils. The mass flux of DDTs in agricultural soil in Zhejiang was calculated to be 43 ng m^{-2} h^{-1} using eq 3 with $k_v = 7.19 \times 10^{-6}$ h^{-1}, which corresponds to a half-life of 11 years.[29] Considering the fact that the residues of DDTs in the southern United States were 27 ng g^{-1}, the data are comparable with that in the southern United States, which was about 9.0 ng m^{-2} h^{-1}. It is worthwhile to note that this mass flux is about 1 order of magnitude lower than that estimated for southern Ontario, Canada (i.e., 188 ng m^{-2} h^{-1}),[28] although the concentration of DDTs in Zhejiang

province (i.e., 82 ng g^{-1} dw) is 2 orders of magnitude lower than that in Ontario (19000 ng g^{-1} dw).[28] This can be explained by the higher temperature and lower soil TOC in the Zhejiang province. The result implies that volatilization of DDTs from soil is more easily accomplished under the condition of high temperature and low soil TOC than under low temperature and high soil TOC. A previous study suggested that the potency of volatility was similar to that of bioaccessibility for POPs.[36] POPs are more accessible by the microbial communities in soils with high temperature and low TOC because of high microbial activity and extractability. The results in the present study indicate that DDTs have a higher volatility in the region with higher temperature and lower TOC. The finding demonstrates the suggestion in previous work.[36] Mass flux of DDTs in Zhejiang soil from 1990 to 2010 is presented in Figure SI-3 of the Supporting Information, indicating that the mass flux of DDTs in Zhejiang soil decreased from 0.0013 g m^{-2} year^{-1} in 1990 to 0.0003 g m^{-2} year^{-1} in 2010. On the basis of the fact that the total cropland in Zhejiang province was 2,000,000 ha (http://www.zj.gov.cn/gb/zjnew/), we can calculate the historical DDT residues and emissions from cropland soil in Zhejiang province (see Figure SI-4 in the Supporting Information). In 2006, 485 tons of DDTs was left in soil, of 7.6 tons was emitted to air, leading to an emission factor of 1.6%.

Component Ratios of DDTs. The fresh DDTs have stable component ratios of 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, <0.5% p,p'-DDD, <0.5% o,p'-DDD, <0.5% o,p'-DDE,

and <0.5% unidentified compounds.[37] After introduction of DDTs into the environment, DDT can be degraded to DDE under aerobic conditions and to DDD under anaerobic conditions by microorganisms.[38,39] Thus, the component ratios can be used to identify sources of DDTs. The ratio of p,p'-DDT/p,p'-DDE was variable in the present study, ranging from 0 to 3.5 and, therefore, much lower than the ratio for fresh DDTs (i.e., 15). This indicates that the DDT residues originated from historical usage and not from recent inputs of DDTs. It is worth noting that the ratio of o,p'-DDT/p,p'-DDT ranging from 0.23 to 3.9 in 95% of the samples was higher than that of o,p'-DDT/p,p'-DDT for fresh DDTs (i.e., 0.2). This suggests a recent application of dicofol, which contains impurities with a much higher amount of o,p'-DDT than p,p'-DDT, because the degradation difference between o,p'-DDT and p,p'-DDT cannot lead to such high ratios of o,p'-DDT/p,p'-DDT.[22] This is in agreement with a previous study in which dicofol was identified as the contamination source of DDTs in air in the Tai Lake region (located in the northern part of Zhejiang Pprovince), where the ratio of o,p'-DDT/p,p'-DDT was higher (i.e., 6.3 ± 3.7) than that in fresh DDTs.[40] Thus, it is very likely that dicofol applied in the province has contributed a certain amount of DDTs (o,p'-DDT in particular) in soil in our study region.

Enantiomeric Composition of o,p'-DDT and o,p'-DDD. The EF distribution of o,p'-DDD and o,p'-DDT is shown in Table 2. Among 46 samples that had sufficient o,p'-DDT levels for the analysis of their EFs, the EFs of 20% of soil samples were not significantly different from racemic o,p'-DDT standard ($p > 0.05$, t test). Forty-eight percent of the EF values ranged between 0.175 and 0.486, indicating that the (+)-o,p'-DDT enantiomer preferentially degraded, whereas 32% of the EF values ranged between 0.534 and 0.892, which was a result of selective depletion of (−)-o,p'-DDT. The EF values were similar to reported values worldwide,[20] U.S. Corn Belt,[25] Fraser Valley of British Columbia, Canada,[41] and Hawaii and Alabama in the Unites States,[42] showing a concurrent existence of racemic and nonracemic residues in soil samples. This implies different microbial communities were dominant at different sites of each of the regions, because only microbial degradation of chiral pollutants is thought to be enantioselective. The minimum EF value of 0.175 in this study was slightly higher than that of 0.154 in soils from the Pearl River Delta,[22] whereas the maximum EF value of 0.892 was slightly higher than that of 0.801 in global background soils.[20] If DEVrac is defined as the absolute value of EFs of chiral compounds subtracted from 0.5,[20] it is interesting to note that a significant negative correlation (F test) was observed between o,p'-DDT/p,p'-DDT and DEVrac of o,p'-DDT in the soil samples ($n = 39$, $r = 0.36$, $p = 0.02$, F test, Figure 2). This indicates the use of dicofol in the Zhejiang region after the ban of large-scale use of DDTs in agriculture, because DEVrac of o,p'-DDT is thought to be smaller in fresh dicofol than in aged DDTs.[22]

The enantioselective degradation of o,p'-DDD was different from the EF distribution of o,p'-DDT. Sixty-two percent (i.e., 29 samples) of the EF values were below 0.5, whereas 38% of the EF values (i.e., 18 samples) were above 0.5. Data on EFs of o,p'-DDD in environmental matrices are limited. To our knowledge, there are only three studies that investigated the EFs of o,p'-DDD in environmental matrix including soil,[30] atmosphere,[43] and sediment.[44] In the previous studies the EFs of o,p'-DDD in the atmosphere in Arkansas (United States)[43] and soil in the Czech Republic and the Sultanate of Oman[30]
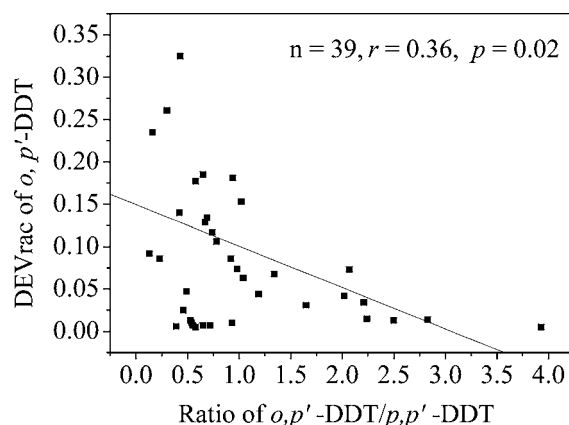

Figure 2. Correlation between ratio of o,p'-DDT/p,p'-DDT and DEVrac of o,p'-DDT (F test).

were calculated from the area of the earlier eluting GC peak divided by the total area of the two peaks, because enantio-enriched standards of o,p'-DDD were not available during that time. In this study, the EFs were calculated by the peak area of the (+)-enantiomer divided by the sum peak area of the (+)- and (−)-enantiomers. However, the calculation method of EFs in the previous works[30,43] should be the same as that in our work, because it has been demonstrated that the (+)-enantiomer of o,p'-DDD elutes first on the chiral stationary phase, which was used in these works.[21] This makes it feasible to compare the EFs of o,p'-DDD in agricultural soil in Zhejiang with those in soil from the Czech Republic and the Sultanate of Oman,[30] the atmosphere in Arkansas,[42] and sediments from Yueqing Bay and Sanmen Bay, East China Sea.[44] The EFs of o,p'-DDD in soil from the Czech Republic and the Sultanate of Oman and the atmosphere in Arkansas scattered around 0.5, similar to the EF distribution pattern in agricultural soil from Zhejiang. In contrast, the EFs of o,p'-DDD were below 0.5 in all sediments from Yueqing Bay and Sanmen Bay, East China Sea,[44] which indicates that the enantioselective degradation of o,p'-DDD in sea sediment might be much different from that in other environmental matrices.

Influence of the Soil Properties on the DDT Concentrations. The correlations between soil properties and the DDT concentrations and also between soil properties and DEVrac of chiral DDTs were investigated, and the significance of all correlations was tested by F test (Table 3). The concentrations of DDTs were significantly positively correlated with the TOC ($p = 0.006$) and microbial biomass carbon (C_{bio}) ($p = 0.03$) but not with the DEVrac of chiral DDTs ($p > 0.05$). This strongly demonstrates that the organochlorine pesticides are more persistent in soils with high organic matter content than in soils with low organic matter content.[25,28] It is interesting to note that the soil C_{bio} was significantly positively correlated with the ratio of p,p'-DDE/p,p'-DDT ($p = 0.02$), but not with the ratio of o,p'-DDD/o,p'-DDT ($p = 0.55$). The former can be explained by the fact that p,p'-DDE is the main metabolic product of p,p'-DDT and the metabolism is predominately controlled by microbes in soil. Although the degradation of o,p'-DDT to o,p'-DDD also depends on the soil C_{bio}, the overlap of the fresh input of o,p'-DDT to the soil due to the fresh application of dicofol and aged o,p'-DDT from historical application of DDT leads to a rather random relationship between soil C_{bio} and the ratio of o,p'-DDD/o,p'-DDT.

Table 3. Correlations between Concentrations of DDTs, Isomer Ratios, and DEVrac of DDTs and Soil Properties (F Test)

	$r (p)^a$				
	TOC	C_{bio}	pH	silt	clay
concentrations of DDTs (ng g^{-1} dw)	0.35 (0.006)P	0.25 (0.03)P	0.19 (0.08)	0.21 (0.06)	0.17 (0.10)
p,p'-DDE/p,p'-DDT	0.21 (0.06)	0.28 (0.02)P	0.13 (0.16)	0.21 (0.06)	0.13 (0.17)
o,p'-DDD/o,p'-DDT	0.21 (0.06)	0.11 (0.55)	0.11 (0.56)	0.21 (0.06)	0.13 (0.74)
DEVrac of o,p'-DDD	0.42 (0.002)N	0.25 (0.05)N	0.42 (0.001)N	0.26 (0.04)N	0.09 (0.25)
DEVrac of o,p'-DDT	0.07 (0.39)	0.11 (0.20)	0.20 (0.10)	0.23 (0.06)	0.15 (0.08)

^{a}P, significant positive correlation; N, significant negative correlation.

With respect to chiral properties, DEVrac of o,p'-DDD was significantly related with most physicochemical and microbial soil properties except with the percentage content of clay (Table 3). The high significant correlation between soil pH and DEVrac of o,p'-DDD ($p < 0.001$) indicates that the pH is an important factor affecting the DEVrac of o,p'-DDD. In contrast, the DEVrac of o,p'-DDT was not significantly correlated with any soil properties ($p > 0.05$).

Implications of the Correlations of the DDT Residue Patterns. There are two distribution patterns of chemicals, the "primary distribution" pattern and the "secondary distribution" pattern.[45,46] The significant correlation between concentrations of DDTs in soil and TOC in this study indicates that the distribution of DDTs is a typical secondary distribution pattern dominated by TOC. Our previous study demonstrated that the distribution of HCHs in the region was also a typical secondary distribution pattern.[31] However, the secondary distribution pattern of HCHs was mainly controlled by the temperature. On the basis of the results presented here and in our previous study,[31] we suggest that the secondary distribution pattern for chemicals which have low vapor pressures (for example, DDT) is driven by TOC, whereas the secondary distribution pattern for chemicals which have high vapor pressures (for example, α-HCH) is driven by temperature.

The fact that p,p'-DDT was significantly positively correlated with p,p'-DDE ($p < 0.0001$) but not with p,p'-DDD ($p = 0.76$) indicates that p,p'-DDE is the main metabolic product of p,p'-DDT in agricultural soils in Zhejiang (Table SI-3 in the Supporting Information). This is consistent with the findings of higher concentrations of p,p'-DDE compared to p,p'-DDD at most of the sites (Table SI-2 in the Supporting Information). This is also supported by the fact that the agricultural soil in Zhejiang is mainly under aerobic conditions at which p,p'-DDT degrades predominantly to p,p'-DDE. The significant correlation of the ratio of p,p'-DDE/p,p'-DDT to soil C_{bio} indicates that the metabolism of p,p'-DDT to p,p'-DDE is predominantly influenced by biochemical and not physicochemical processes.

Previous laboratory studies demonstrated that enantioselective degradation of chiral contaminants is highly influenced by the soil pH.[47,48] The high significant negative correlation ($p < 0.001$) between DEVrac of o,p'-DDD and pH supports the hypothesis that the pH is an important factor in the enantioselective degradation of chiral contaminants, implying that low soil pH is favorable to the formation and/or the activity improvement of the bacteria community, which can enantioselectively degrade o,p'-DDD.

Overall, the present study shows the level of residues were similar to those reported in the Pearl River Delta, Tianjin, and Haihe plain in China, but higher than those in agricultural soils from the U.S. Corn Belt and lower than those in agricultural soils from southern Ontario in Canada. Compared with southern Ontario, Canada, Zhejiang has a high volatilization

rate of DDTs, which was due to higher temperature and lower soil TOC in Zhejiang. The results imply the global distribution of DDTs might exhibit the trend with high concentrations in areas with low temperature and high TOC and low concentrations in areas with high temperature and low TOC with the time proceeding. In 2006, 485 tons of DDTs was left in soil in Zhejiang, of which 7.6 tons was volatilized to air, leading to a volatilization factor of 1.6%. The ratio of o,p'-DDD/p,p'-DDD indicates the residues of DDTs in agricultural soil in Zhejiang were from both DDTs and dicofol application. The distribution showed a typical secondary distribution pattern of DDTs in agricultural soil influenced by soil TOC, not temperature and usage. The high significant negative correlation ($p < 0.001$) between DEVrac of o,p'-DDD and pH suggested that low soil pH is favorable to the formation and/or the activity improvement of the bacteria community, which can enantioselectively degrade o,p'-DDD. The observations highlight key factors (i.e., soil TOC and pH) that control the distribution pattern and enantioselective degradation of DDTs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data on sampling, concentrations of DDTs, mass flux of DDTs, and residues and emissions of DDTs in agricultural soil in Zhejiang. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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