

# Adsorption Characteristics and Mechanisms of Organochlorine Pesticide DDT on Farmland Soils

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## Abstract

The adsorption behavior and the adsorption mechanism of the persistent organic pollutant DDT existing extensively in soils around the world are the key to solve the DDT-contaminated soils. Hence, in this paper, selective extraction and batch experimental method were used to examine the adsorption of DDT on farmland soils H and S in Northeast China. Simultaneously, the parameters indicating soil properties and composition such as soil particle, organic matter, and minerals, ect. were analyzed. Results show that the shape and the best fitted model of adsorption isotherm of DDT in both soils were L-type and Freundlich model, respectively. Smaller soil particle had greater adsorption capacity to DDT. The effects of organic matter and minerals on the adsorption of DDT were related to the composition and the origin of organic matter and minerals. Both SiO<sub>2</sub> and illite-montmorillonite mixed-layer could hardly adsorb DDT, and the iron oxides could adsorb DDT, while the function of manganese oxides was inhibitory of DDT adsorption. Organic matter had greater adsorption capacity to DDT than iron oxides. The adsorption capacity of the plant residues is the greatest, followed by the aromatic substances from the plant and the products from microbial degradation.

**Keywords:** adsorption, mechanism, DDT, soil, organic matter, minerals

## Introduction

Soil contamination by persistent organic pollutants (POPs) is an environmental problem worldwide. Organochlorine pesticide DDT (dichlorodiphenyl-trichloroethane), as an important persistent organic pollutant [1], is still used in some countries [2] and widely exists in soils with high concentration around the world [3-7] due to its persistence in the environment, bioaccumulation, and long-distance transportation [8], although it has been banned for several decades. Therefore, how to efficiently solve DDT contamination in soils has been drawing much scientific and public attention.

In general, various environmental behaviors of pesticides entering soils will take place, including adsorption, desorption, degradation, volatilization, plant uptake [9], diffusion, and so on. Among these behaviors, adsorption of pesticides is an important process, affecting all other environmental behaviors and determining the final fate of these pollutants in soil [10-13] and the feasibility of a remediation technique on the pesticide-contaminated soil. Therefore, knowledge of the adsorption characteristics of DDT and its relevant mechanisms is important for revealing the mechanisms of other environmental behaviors and restoring DDT-contaminated soils.

Physicochemical properties and material compositions of soils have complicated influences on the adsorption of organic pollutants on soils. Even for the same organic pes-

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ticide, the same components and properties of soils may generate different effects on its adsorption behavior. For instance, the adsorptions of Glyphosate (GPS) [14, 15], Terbutylazine [16], and Prometryne [17] were highly correlated with the contents of soil organic matters, whereas Gerritse et al. [18], Dousset et al. [19], and Oliver et al. [20] found that organic matters of soils had little effects on them. Adsorption of GPS [21] and diuron [22] on soils generally decreased as the pH values of soils increased, however, other studies have considered that GPS [23, 24] and diuron [25] were independent of soil pH. The differences among these research results might result from the humified degree of the soil organic matters [26] and pesticide acidity (pKa) and base (pKb) constants [27]. Additionally, the effect of the same soil composition on the adsorption of different pesticides produces different results. Yu and Zhou pointed out that soil minerals can provide more available adsorption sites for methamidophos (MDP) than for GPS [28]. Therefore, these results indicate that adsorption behavior of pesticides also depends on the pesticide properties, except for the properties and composition of soils. Water solubility of pesticides has an important effect on their sorption [29]. Hydrophobicity, structure, and composition of the pesticides are associated with their adsorption behavior.

DDT is a condensation compound from chlorobenzene and trichloroacetaldehyde in the presence of concentrated sulfuric acid, and has its own characteristics. Thus it can be concluded that the adsorption behavior of DDT in soils should have its own adsorption characteristics and mechanisms. By now, the adsorption of DDT on soils/sediments also has been studied. The adsorption abilities of DDT on both soil and sediment were significantly different, and the sequence of adsorption abilities was organic soil, stream sediment, Beverly sandy loam, and Zplain field [30, 31]. The adsorption amount of DDT onto the primary clay was lower than that of organoclays [32]. Although these results can provide some information of the adsorption of DDT in soil, little has been known about the adsorption mechanism of DDT on soils.

Northeast China is one of China's major grain production bases with its fertile soils guaranteeing food production. Long-term food production inevitably gives rise to pesticide residues in soil, and DDT can still be detected in these arable soils now. Consequently, it is necessary to study the adsorption behavior of DDT in these soils in order to offer some information for restoring the DDT-contaminated soils and ensuring food security. So far, few studies have been reported about the adsorption behavior of DDT on the soils in Northeast China. Black soil and sandy soil, significantly different in the properties and the components, are two types of agricultural soils in Northeast China. Hence, in this work, black soil and sandy soil were selected to study the adsorption thermodynamic characteristics and mechanisms of DDT on them. This research includes the following three parts:

- (1) The adsorption characteristics of DDT onto these two soils
- (2) The relationship of the adsorption of DDT with soil properties, organic matter, and minerals

- (3) The effects of composition and origin of organic matter and minerals on the adsorption of DDT.

## Materials and Methods

### Materials

#### *Collection and Treatment of Soil Samples*

Soil samples were collected from the top 0-20 cm of the soil surface from farmland at two locations of Changchun suburb (black soil, signified as H) and Nong'an County (sandy soil, signified as S), Jilin Province, China. After the removal of sundries such as gravel, deadwood, rotten leaves, and so on, the soils were subsequently air-dried and passed through 2 mm and 0.25 mm mesh sieves in order to improve the homogeneity of soil samples. The contents of organic matters in soil H and soil S were 1511 and 638.99  $\mu\text{mol/g}$ , respectively, determined by a TOC analyzer (TOC-5000A, Shimadzu, Japan). The pH values of soil H and soil S were 6.86 and 6.83, respectively, measured at a 1:2.5 (W/W) soil/water ratio using a glass electrode. Particle size analysis was performed by the sieve pipette method, and soil H contained 76.71% sand, 17.61% silt, and 5.68% clay; soil S contained 95.79% sand, 3.54% silt, and 0.67% clay. The cation exchange capacities (CEC) of soil H and soil S were 28.67 and 11.77 c mol/kg, respectively, determined by the ammonium acetate method.

Subsamples, including organic matter-removed soils (HOM and SOM), manganese oxide-removed soils (HMn and SMn), and iron and manganese oxide-removed soils (HFM and SFM) were prepared with the selected extraction method [33]. The concentrations and extraction ratios of organic matter, manganese oxides, and iron oxides in the original soils and the subsamples were determined by the combination of selected extraction method and improved Tessier's sequential extraction method, and results are summarized in Table 1. The organic matters of sand, silt, and clay in soils were removed using the same extraction method.

The samples of original soils and organic matter-removed soils were identified by the X-ray diffraction technique using a Rigaku D/max-2550 apparatus (Japan).

#### *Chemical*

*P,p'*-DDT (1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane) as the representative DDT of model POPs was selected in this work, which was purchased from Dr. Ehrenstorfer (Germany) with purity of 99.5%.

#### *Adsorption Experiments*

Adsorption experiments were conducted in triplicate with the batch experimental method for the prepared soil samples with an adsorbent quantity of 0.0200 g together with technical DDT concentrations of 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0  $\mu\text{g/L}$  in an Erlenmeyer flask fully con-

Table 1. Main chemical compositions in original soils of H and S and before and after selected extraction.

Composition	Original soil	Manganese oxides-removed soil		Iron and manganese oxides-removed soil		Organic matter-removed soil		Total extractable state	
	Content	Content	Extraction ratio	Content	Extraction ratio	Content	Extraction ratio		
H	Fe oxides	745.80	256.86	20.30	131.89	59.08	298.58	7.35	322.28
	Mn oxides	77.18	16.30	63.33	25.37	42.93	39.60	10.89	44.44
	Organic matter	1511.26	1402.79	3.28	1394.66	3.84	455.27	68.61	1450.41
S	Fe oxides	315.34	108.25	21.26	54.25	60.54	119.85	12.82	137.48
	Mn oxides	32.634	6.87	63.78	10.43	44.96	15.90	16.15	18.96
	Organic matter	638.99	591.17	4.45	573.69	7.28	182.75	70.46	618.70

The concentrations of iron oxides and manganese oxides in all soil samples are signified by the concentrations of Fe and Mn, and units of concentrations and extraction ratios of all compositions are  $\mu\text{mol/g}$  and %, respectively.

taining distilled water with 100 mg/L  $\text{NaN}_3$ . The blank experiments were performed to determine the influence of the Erlenmeyer flask and DDT from soil samples on DDT adsorption. These adsorption samples were then equilibrated in a reciprocating shaker shielded from light for 48 h at  $25 \pm 1^\circ\text{C}$  and were subsequently centrifuged at 3,800 rpm for 30 min. The suspension was prepared by the solid phase extraction (SPE) through C18 cartridges (500 mg/6 mL from Agilent, USA) after filtration (0.45  $\mu\text{m}$  GF filter, Whatman, USA), and the concentrations of DDT in solution were analyzed by GC. The adsorbed DDT amount was calculated from the difference between the initial and final concentrations after reaching equilibrium.

#### Analysis of DDT

Analysis was performed using a SHIMADZU (GC-2010) gas chromatograph equipped with an electron capture detector (ECD) and a DB-5 capillary column (30 m, 0.25 mm i.d. and 0.25  $\mu\text{m}$  film thickness). High-purity nitrogen was used as the carrier gas at a flow rate of 9.4 mL/min with the injector and detector temperatures at  $250^\circ\text{C}$  and  $280^\circ\text{C}$ ,

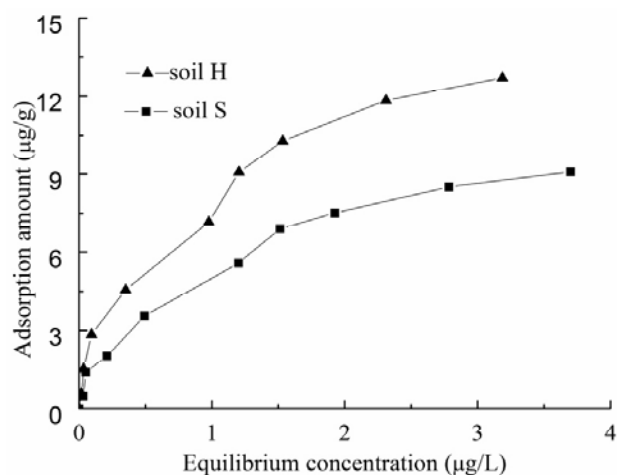


Fig. 1. Adsorption thermodynamics isotherms of DDT on soil H and S.

respectively. Oven temperature was programmed to start at  $100^\circ\text{C}$  with heating at  $20^\circ\text{C}/\text{min}$  to  $210^\circ\text{C}$ , then increased at  $10^\circ\text{C}/\text{min}$  to  $250^\circ\text{C}$  (10 min). A 1  $\mu\text{L}$  sample was injected splitless. In this method, the detection limit of *p*, *p'*-DDT was 0.1 ng/L. *p*, *p'*-DDT recoveries were 80-103%, and the relative standard deviation was 4.8%.

#### Data Evaluation

Adsorption isotherm parameters were calculated for all soil samples by the Langmuir, Freundlich, and Linear (Henry) equations, and their mathematical expressions and meaning of parameters were introduced by Seiichi et al. [34].

## Results and Discussions

### Characteristics of DDT Adsorption Thermodynamics

Fig. 1 shows the adsorption isotherms of DDT on soils H and S. As shown in Fig. 1, the adsorption thermodynamic processes of DDT on soils H and S within the experimental concentration ranges of DDT were similar. With the increase of the equilibrium concentration, the adsorption amounts of DDT on both soils showed an increasing trend, but did not reach the maximums. At the same equilibrium concentration, the adsorption of DDT on soil H was greater than that on soil S, and there was a significant difference between them ( $P < 0.01$ ). This indicated that the adsorption capacity of soil H to DDT was greater than that of soil S. The shape of both adsorption isotherms showed as L-shape, including an initial linear increase and followed by nonlinear increase, and their slopes tended to become smaller.

The effect of DDT initial concentration on the adsorption ratio of DDT on soils is listed in Fig. 2. Although there was difference in adsorption ratio between soil H with the range of 36.29-81.88% and soil S with the range of 25.99-68.12%, the shape of both adsorption ratio curves was the

Table 2. Model parameters, correlation coefficients, and standard deviations for adsorption of DDT on the soils and their compositions.

	Langmuir				Freundlich				Henry		
	$Q_{max}$ ug/g	$b_L$	$R$	$SE$	$K_f$	$1/n$	$R$	$SE$	$K_d$	$R$	$SE$
H	14.104	2.555	0.980	0.668	7.771	0.546	0.980	0.104	4.076	0.941	0.905
HOM	13.089	2.227	0.977	0.543	6.392	0.554	0.979	0.118	3.336	0.929	1.017
HMn	19.084	2.633	0.963	0.593	12.018	0.604	0.983	0.111	6.485	0.922	1.492
HFM	16.051	2.596	0.972	0.764	8.962	0.551	0.977	1.881	4.043	0.907	1.203
S	9.461	1.908	0.956	0.384	4.987	0.567	0.978	0.094	2.509	0.941	0.609
SOM	6.173	1.521	0.982	0.276	2.921	0.578	0.984	0.848	1.413	0.955	0.346
SMn	11.723	2.487	0.957	0.411	6.856	0.559	0.979	1.610	3.126	0.912	0.988
SFM	10.526	2.004	0.969	0.269	5.596	0.562	0.977	1.417	2.379	0.893	0.897

$R_{0.05(9-2)}=0.6664$ ;  $R_{0.01(9-2)}=0.7977$ . In the table, H and S represent soil H and soil S; HOM and SOM represent organic matter-removed soil H and soil S, respectively; HMn and SMn represent manganese oxide-removed soil H and soil S, respectively; and HFM and SFM represent iron and manganese oxide-removed soil H and soil S, respectively.

same in the initial concentration range of DDT (Fig. 2). As the initial concentration of DDT increased, the adsorption ratios of DDT onto both soils firstly increased then decreased, achieving the maximums of 86.8% in soil H and 79.2% in soil S at the initial concentration of 0.25  $\mu\text{g/L}$ . It indicated that the adsorption capacities of soils to DDT were high as DDT initial concentration was low, whereas the adsorption capacities were low as DDT initial concentration was high. At the same initial concentration, the adsorption ratio of DDT on soil H was higher than that on soil S, which further confirmed that soil H had larger adsorption capacity than soil S.

The adsorption thermodynamic processes of DDT onto soils were fitted by Langmuir, Freundlich, and Henry models, and the correlation coefficients and the constants from these models are shown in Table 2. The correlation coefficient  $R$  and the standard error  $SE$  are important parameters to evaluate the fitting effects between experimental data of adsorption and models, and a greater  $R$  and a smaller  $SE$  show a better fitting effect [35]. It could be seen from Table 2 that all the adsorption models could describe the adsorption thermodynamic processes of DDT on soil H and S well, in which the Freundlich model fitted best, followed by Langmuir model. This indicated that surface adsorption and partition adsorption simultaneously took place in adsorption thermodynamic processes of DDT due to soil heterogeneity.

The Freundlich model can be applied to describe multi-layer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Freundlich, 1906) [36].  $K_f$  and  $n$  are the Freundlich constants, and  $K_f$  is an indicator of adsorption capacity of soils to pollutants, and  $n$  refers to adsorption intensity of soils to pollutants. The higher the parameters  $K_f$  and  $n$  are, the greater the adsorption capacity and intensity of soil to DDT will become [37]. According to the values of  $K_f$  and  $n$  in Table 2, the adsorption capacity and intensity of soil H to DDT were higher than those of soil S. In addition, it could

be inferred from  $1/n$  values that these adsorption isotherms were L-type ( $1/n < 1$ ), the same as the above results, indicating minimum competition between DDT and water molecules for adsorption sites on soils [38]. The Langmuir model assumes monolayer coverage of adsorbate over a homogenous adsorbent surface (Langmuir, 1918) [39]. In the Langmuir model,  $Q_{max}$  and  $b_L$  are the Langmuir constants, representing the monolayer adsorption capacity and the affinity between adsorbent and adsorbate, respectively. Observed from Table 2, the monolayer adsorption capacity and the affinity of soil H to DDT were greater than those of soil S, which was similar to the results from Fig. 1 and the Freundlich model. The product of  $Q_{max}$  and  $b_L$  ( $\text{MEC}=Q_{max} \times b_L$ ) in Langmuir model represents the maximum environmental capacity of soil to pollutants, which indicates that the soil environment can accommodate maximum of pollutant load. Soil H can accommodate more DDT than soil S because the MEC of soil H with 35.971  $\mu\text{g/g}$  was higher than that of soil S with 18.050  $\mu\text{g/g}$ . The

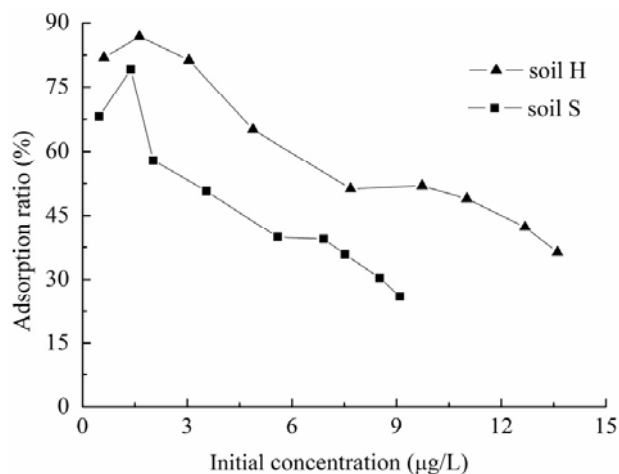


Fig. 2. The relationship between the adsorption ratio of DDT and DDT initial concentration.

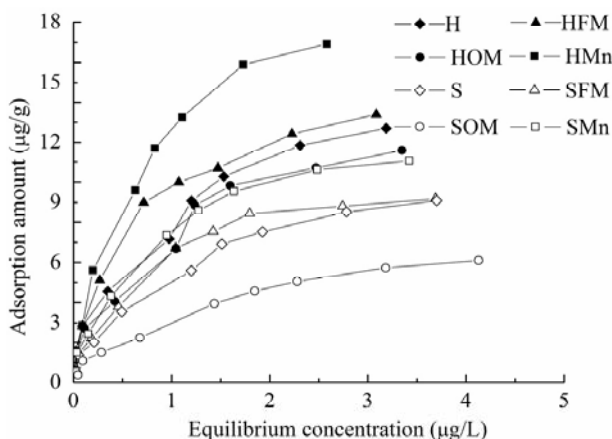


Fig. 3. Adsorption thermodynamics curves of DDT on different soil samples.

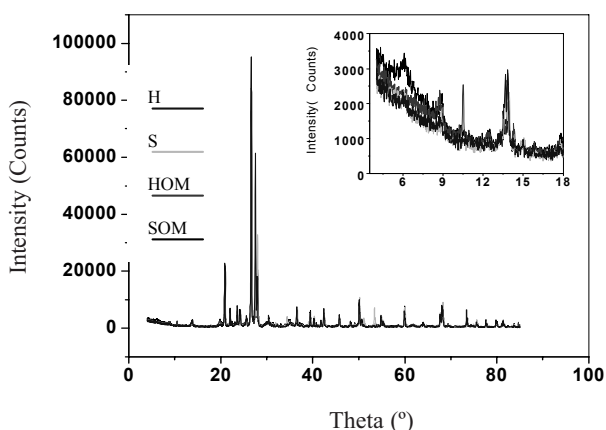


Fig. 4. XRD spectrum of original soils and organic matter-removed soils.

adsorption isotherms were almost linear when the equilibrium concentrations of DDT were below 1.532  $\mu\text{g/L}$  in soil H and 1.925  $\mu\text{g/L}$  in soil S, which showed the partition adsorption played a key role at this stage. It might also explain why the DDT adsorption isotherms conformed so well to the Henry equation in the experimental concentration range of DDT.

Constant  $K_d$  in the Henry model, as a partition coefficient of DDT between solid phase and liquid phase, indicates the adsorption capacity of soil to DDT. A larger  $K_d$  value means the stronger adsorption capacity of soil to DDT. The  $K_d$  in soil H was greater than that in soil S (Table 2), which implied the adsorption capacity of soil H to DDT was greater than that of soil S in the partition adsorption process of DDT.

### Effects of Soil Properties and Compositions on DDT Adsorption

#### *Soil Properties*

Physical and chemical properties of soils are important factors affecting the adsorption of organic pollutants on soils. The organic matter content, particulate distribution,

ionic strength, and pH could influence the adsorption of DDTs on soils [40]. Hamaker and Tompson pointed out that organic matter of soils plays a vital role in the adsorption of organic pollutants [41], especially DDT, because soil organic matter caused both partition adsorption through dissolution and surface adsorption through the combination of special sites in humic acid structure with DDT. Both adsorption mechanisms became more remarkable with the increase of the content of soil organic matter. This may explain why the adsorption thermodynamic processes of DDT on soil H and S could well be described by the non-linear equations and the linear equation. The adsorption capacity, intensity and affinity of soil H to DDT were greater than those of soil S because the content of organic matter in soil H was almost 2.5 times as much as that in soil S.

The adsorption capacity of organic pollutants on soils is generally negatively correlated with particle size [42]. In this study, the adsorption amounts of DDT on sand, silt and clay were 4.699, 5.269, and 6.065  $\mu\text{g/g}$ , respectively, which were consistent with the result of Zhou et al. [42]. Thus it could be inferred that the soil with the higher contents of clay and silt would have stronger adsorption capacity. The contents of silt and clay in soil H were 4 times and 7.5 times higher than those of soil S, respectively, which also resulted in soil H having stronger adsorption capacity to DDT than soil S.

Huang et al. [43] found that minerals and organic matter in soils were important materials in the adsorption process of the hydrophobic organic pollutants on soils. Organic matter and inorganic minerals from soil particles certainly play important roles in the adsorption of organic pollutants on soil. In order to reveal the effects of organic matter and minerals from soil particles on DDT adsorption, the organic matters of three soil particles were removed, correspondingly forming three subsamples of organic matter-removed sand, organic matter-removed silt and organic matter-removed clay. And then these subsamples and original particles were used to adsorb DDT. The adsorption amounts of DDT on these subsamples followed the order of organic matter-removed sand with adsorption amount of 2.767  $\mu\text{g/g}$  < organic matter-removed silt with adsorption amount of 3.966  $\mu\text{g/g}$  < organic matter-removed clay with adsorption amount of 4.674  $\mu\text{g/g}$ . Compared to the adsorption amounts of original particles, the adsorption amounts of DDT on organic matter-removed particles were declined by 41.12% (sand), 24.72% (silt), and 22.93% (clay), respectively. It implied that the minerals from different soil particles had different adsorption capacities to DDT and followed the sequence of clay mineral > silt mineral > sand mineral. However, the adsorption capacities of DDT on organic matters of these particles are presented in reverse order. It was reported that there were obvious differences in the organic composition of sand, silt and clay particles, i.e., plant debris in sand particles, aromatic substances from plants in silt particles, and products from microbiological degradation in clay particles [44]. Furthermore, sand and silt particles are made up of primary minerals quartz and feldspar, and clay particles of secondary minerals, includ-

ing silicate, goethite and hematite, montmorillonite, iron oxides, manganese oxides, illite, etc. Hence, according to the above facts, the following conclusions could be inferred:

- (1) The sequence of the adsorption capacities of DDT on organic matters of soil particles was the plant residues > the aromatic substances from the plant > the products from microbial degradation.
- (2) The secondary minerals such as goethite and hematite had greater adsorption capacities to DDT than the primary minerals.
- (3) In clay and silt particles, the adsorption capacities of minerals were better than those of organic matter, but in sand particles their adsorption capacities were similar.

There was no significant difference in pH value between soil H and soil S. This indicated adsorption differences caused by pH between soil H and soil S should not be taken into account. Although the cation exchange capacity of soil H was much larger than that of soil S, it did not lead to adsorption differences between both soils because DDT as a weak polar non-ionic organics, existing mainly in a molecular state in solution, could hardly be adsorbed by exchange interaction.

### Soil Compositions

Observed from Table 1, the contents of organic matter, iron, and manganese oxides in soil H were approximately twice those of soil S, which may lead to the result that the adsorption capacity of soil H was greater than that of soil S. In order to verify this inference, these components were removed from soils using the selection extraction method, and then the adsorption characteristics of DDT on the residuals were investigated. These results are shown in both Table 2 and Fig. 3.

It has been reported that the non-target component can be simultaneously extracted when the target component is extracted using an extracting agent. When manganese oxides were regarded as the extracted target in both soils, their extraction ratios were up to 64% while organic matter and iron oxides as non-target components were simultaneously extracted out about 4% and 21%, respectively (Table 2). The higher extraction of non-target extracted iron oxides in the extracted process of manganese oxides was mainly related with iron oxide forms in soils. Li et al. pointed out that although extracting agent  $\text{NH}_2\text{OH}\cdot\text{HCl}$  could selectively extract amorphous manganese oxides, it could also take out part of the amorphous iron oxides and carbonate fraction of Fe in the soil/sediment [45]. When iron and manganese oxides were extracted and separated from soils using an extracting agent, the extraction ratios of both iron oxides and manganese oxides exceeded 40%, meanwhile almost 4% of non-target component organic matter was removed. The extraction ratio of organic matter was relatively high and close to 70%, and about 10% of non-target iron oxide component and manganese oxides were simultaneously removed. Additionally, the extraction ratios of target and non-target components from soil S were higher than

those of soil H, which indicated that the acting force and strength between the chemical components and soils in various soils were different. Furthermore, it could be seen that the extraction ratios of non-target components were relatively low and thus could be ignored compared with those of target components. Hence, the selective extraction method was feasibly and effectively used to separate the active components of soils.

According to the result of Fig. 3, the shape of the adsorption isotherms of DDT on soil samples removing various components also presented L-type. However, there were obvious differences in the DDT adsorption amounts on these subsamples from soils at the same equilibrium concentration, and the sequence followed was: the manganese oxides-removed soils > iron and manganese oxides-removed soils > organic matter-removed soils. Furthermore, in comparison with those on original soil H and S, the adsorption amounts of DDT on the manganese oxides-removed soils and iron and manganese oxides-removed soils were higher, while those on the organic matter-removed soils were lower.

The Langmuir, Freundlich, and Henry models were used to fit the adsorption data of DDT on subsamples, and the fitting results also are listed in Table 2. According to the values of the correlation coefficient and standard error, these adsorption isothermal models could describe the adsorption thermodynamic processes of DDT on subsamples well, which was consistent with the adsorption characteristics of DDT on original soils of H and S. However, the best fitting models were Freundlich for subsamples from soil H and Langmuir for subsamples from soil S, respectively, because the higher extraction ratios of different components in soil S could reduce the heterogeneity of surface of soil S and, accordingly improve the surface homogeneity of soil S. It could be concluded from these results above that the adsorption mechanisms of both soils did not change as some components of soils were removed, whereas for soil S the dominant adsorption mechanisms changed from the adsorption concerned with heterogeneous surface to monolayer adsorption. Although the maximum adsorption capacities of subsamples from soil H to DDT were far higher than those of subsamples from soil S, the maximum adsorption capacities of these subsamples in both soil H and soil S followed the same sequence as the manganese oxides-removed soils (19.084  $\mu\text{g/g}$  and 11.723  $\mu\text{g/g}$ ) > iron and manganese oxides-removed soils (16.051  $\mu\text{g/g}$  and 10.526  $\mu\text{g/g}$ ) > organic matter-removed soils (13.089  $\mu\text{g/g}$  and 6.173  $\mu\text{g/g}$ ). In addition, according to the values of  $K_f$  from Freundlich model and  $b_L$  from Langmuir model in Table 2, it could also be found that the adsorption capacities and affinities of subsamples from soil H to DDT were higher than those of subsamples from soil S, their sequence was the same as the result from  $Q_{max}$ . These may be attributed to the following result that these soil samples had different contents of organic matters, iron oxides, and manganite oxides. In comparison with those of original soil H and S to DDT, the adsorption capacities and affinities of the manganese oxide-removed soils and iron and manganese oxide-

removed soils to DDT were higher, while those of the organic matter-removed soils were lower. These results indicated that manganese oxides had an inhibitory effect on DDT adsorption, while iron oxides and organic matter promoted DDT adsorption. In order to confirm the relationship between three components and DDT adsorption and reveal the relevant adsorption mechanisms, a multiple regression equation between the constant  $K_f$  and the contents of the three components was established using the multivariate statistics method and the obtained result was  $Y_{KF} = 3.856 + 0.006X_{Fe} - 0.100X_{Mn} + 0.005X_{OM}$  ( $P < 0.05$ ). According to constant values before independent variables in the multiple regression equation, it was found that the results were the same as the above results, i.e., organic matter and iron oxides facilitated DDT adsorption, and manganese oxides restrained DDT adsorption. The effect of iron oxides of unit mass on adsorption was stronger than that of organic matter of unit mass, and the inhibitory effect of manganese oxides of unit mass was far stronger than the promoting effect of iron oxides and organic matter of unit mass. As shown in Table 1, for soils H and S, the contents of the organic matter and iron oxides almost approached 20 times and 10 times as many as those of manganese oxides, hence the inhibitory effect of the latter on the adsorption was covered by the promoting effect of organic matter and iron oxides. In addition, the contents of organic matter in both soils were far higher than those of iron oxides. This indicated that organic matter had higher adsorption capacity than the iron oxides in both adsorption systems of soil H and soil S. And thus it could be confirmed that the higher contents of organic matter and iron oxides in soil H made the adsorption capacity, intensity, and affinity to DDT stronger than those in soil S.

In fact, organic matter has an important role in the adsorption of DDT to soil due to the active functional groups, such as the phenolic group, carbonyl, ethanol carbonyl, methyl and so on, which could cause all kinds of chemical bonds or produce complex ability with DDT. In this study, the contents of organic matter of soil H and S were 1,511.26  $\mu\text{mol/g}$  and 638.99  $\mu\text{mol/g}$ , respectively, which caused the adsorption of DDT on original soils. The contents of the residual organic matter in both subsamples generated by  $\text{H}_2\text{O}_2$  extraction were reduced from 1,511.26  $\mu\text{mol/g}$  and 638.99  $\mu\text{mol/g}$  to 455.27  $\mu\text{mol/g}$ , and 182.75  $\mu\text{mol/g}$ , which obviously led to the decrease of the adsorption capacities, intensities, and affinities of the organic matter-removed soils to DDT.

The iron oxides and manganese oxides belonging to secondary minerals in soil/sediment not only participated in organic pollutant adsorption, but also are potential chemical oxidants. In aerobic condition, high iron oxides and manganese oxides can oxidize organic pollutants and decrease their contents [46]. The contents of iron oxides in both soils were almost 10 times higher than those of manganese oxides, which indicated that the chemical oxidation of DDT caused by manganese oxides could be ignored compared with iron oxides. As the coordination of ion with

manganese oxide surface is unsaturated, manganese oxides can easily be coordinated with the water in soil adsorption system. The coordinated water is dissociated and correspondingly formed the hydroxylation surface on the surface of manganese oxides. Protolysis takes place on hydroxylation surface and accordingly generates amphoteric surface and charge change. Balistrieri and Murray have found that the value of zero charge of manganese oxides is between 1.4 and 2.8 [47]. Therefore, it could be inferred that under the condition of pH of soil H and S,  $\text{Mn}^{2+}$  and its ligand formed by the oxidation of manganese oxides would be adsorbed on the soil surface by the electrostatic interaction, which could lead to the decrease of the adsorption sites, and thus inhibited the adsorption of DDT on soils. However, after the removal of manganese oxides in soils, some new adsorption sites remaining under the cover of manganese oxides will be exposed, which would increase the effective adsorption sites of the manganese oxide-removed soils, and enhance the adsorption of DDT. 40% of manganese oxides were extracted when extracting iron oxides, which could explain why the adsorption amount of DDT on iron and manganese oxide-removed soil was higher than original soil. Iron oxides in soil not only adsorbed and fixed DDT, but also promoted the transformation of DDT. There are a lot of iron oxide forms, and their values of zero charge are between neutral and alkaline. Soils H and S, close to neutral pH, were beneficial to the coordination reaction of soils with DDT molecules, and thus promoted the adsorption effect of DDT on iron oxides.

Mathur and Moudgil found that  $\text{SiO}_2$  had strong affinity to organic pollutants as well [48]. In Fig.4, the sharp peak of  $\text{SiO}_2$  in the X-ray diffraction spectrum indicated the obvious crystallization in soils. There was the largest relative content of  $\text{SiO}_2$  in the organic matter-removed soil H (HOM) by comparatively analyzing the content of  $\text{SiO}_2$  in different soils, including original soils and organic matter-removed soils according to the normal card of XRD (No. 461045). Hence, it could be inferred that HOM should have the highest affinity to DDT of all soil samples. On the contrary, the adsorption of DDT on Soil H was more than that of HOM, which indicated the adsorption of DDT onto soil hardly depended on  $\text{SiO}_2$ . It was known that montmorillonite and illite of soil usually had high affinity to organic pollutants. Therefore, the adsorption capacity of soils to DDT should also be related to relative content of illite-montmorillonite mixed-layer to some extent. The distribution, composition and content of the illite-montmorillonite mixed-layer in clay mineral can be observed within the range of  $\theta \leq 15^\circ$  in Fig. 4, and it was seen that the content order of the illite-montmorillonite mixed-layer was  $\text{SOM} > \text{HOM} > \text{H} > \text{S}$ . However, the adsorption of DDT by the four kinds of soil samples followed the order of  $\text{H} > \text{HOM} > \text{S} > \text{SOM}$ , and the result was not consistent with the contents of illite-montmorillonite mixed-layer in soil samples, which indicated that the illite-montmorillonite mixed-layer had little effect on the adsorption of DDT on soils.

## Conclusion

The adsorption of DDT on soils H and S were well described by the Langmuir, Freundlich, and Henry models, with Freundlich being the best fitted model. The soil properties and composition had important influences on the adsorption of DDT on soils. Smaller particles had greater adsorption capacity to DDT. The adsorption of DDT on soils was related to the composition and origin of organic matter and minerals. The illite-montmorillonite mixed-layer, SiO<sub>2</sub>, iron oxides, and manganese oxides showed different relationships with the adsorption of DDT on soils. The adsorption capacities of different organic matter followed the sequence of the plant residues>the aromatic substances from the plant>the products from microbial degradation.

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