RETRACTED ARTICLE: Adsorption, degradation and leaching migration characteristics of chlorothalonil in different soils

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ABSTRACT
The adsorption, degradation and leaching characteristics of chlorothalonil in two representative soil were studied using simulated soil degradation and soil column leaching. The results showed that the adsorption of chlorothalonil in clay and sandy soil can be characterized by the Freundlich equation. The adsorption coefficient ($K$) was 6.7158 and 1.2568, respectively. Both soils were physical adsorption. The residual degradation kinetics of chlorothalonil in both soils met the first-order kinetics degradation equation. As the concentration of chlorothalonil increased, the higher the residual amount of chlorothalonil in the soil, the slower the degradation rate and the longer the half-life. In the soil column, chlorothalonil was not easy to move and migrate in the two soil columns. The highest residual residues were in the range of 0 to 10 cm (the topmost), and then a decrease in order. The correlation analysis showed that the adsorption and leaching of chlorothalonil in the two soils may be affected by a combination of factors such as soil organic matter content, clay content, cation exchange capacity, and soil pH value, it posed a great risk of groundwater contamination, so should be given serious attention.

Introduction
The problem of pesticide residues has been a hot topic. The residual pollution of pesticides in the environment had attracted more and more attention. Among them, the pollution of groundwater by pesticides was particularly affected according to report by researchers (Kumari & John, 2019; Shokoohi et al., 2019; Xiao et al., 2019). The principal factor affecting the pollution of groundwater by pesticides was the migration and persistence of pesticides in the soil (Hearon et al., 2019; López-Ruiz et al., 2019; Y. C. Sun et al., 2015). The migration of pesticides in the soil was closely related to the water solubility and adsorption characteristics of pesticides and other factors. It was a principal index to assess the ecological environment of pesticides (Duchowicz, 2020; Hearon et al., 2019).

Chlorothalonil (CTN) was a broad-spectrum fungicide widely used in the control of downy mildew, anthracnose, and diseases in various crops, such as fruit and vegetables, cereals, etc. (Jankowska et al., 2016; Teng et al., 2017). It was employed in agricultural production. During the process of spraying, part of the chlorothalonil was directly absorbed by the crop, or the fungicides on the crop surface entered the soil under the action of rain erosion, leaf surface runoff and other factors, and may also directly fall into the soil (Adjailton et al., 2017; Teng et al., 2017). Therefore, it directly led to large residues in fruit, vegetables and the soil, and directly caused serious damage to the ecological environment and human health (Jankowska et al., 2016). In recent years, with the gradual expansion of various fruit and vegetable planting areas, the presence of pesticide residues had become ever more and more common. Studies have shown that chlorothalonil had a strong “triple effect” and was severely irritated to the skin, eyes and stomach. And chlorothalonil had good adhesiveness on the surface of plants and was not easily washed by rainwater, resistance to light, long residual period and other characteristics. Mustachio (Mozzachio et al., 2008) found that chlorothalonil was associated with carcinogenicity due to its toxicity. Lopes (Lopes et al., 2020) found that chlorothalonil can be considered as a toxic compound for fish, causing genotoxicity and affecting the RBCs physiology and the fertility of males of P. vivipara. Therefore, the harm of chlorothalonil had drawn more and more attention (Que & Zainal, 2010). H. T. Li et al. (2020) demonstrated that carbendazim (CBZ) and chlorothalonil (Chl) together synergize to decrease sperm motility in vitro (CBZ 1.0 + Chl 0.1, CBZ 10.0 + CHL 1.0, CBZ 100.0 + Chl 10 μM in incubation medium for 24 h) and sperm concentration and motility in vivo with ICR mice (CBZ 0.1 + Chl 0.1, CBZ 1.0 + CHI 1.0, CBZ 10.0 + Chl...
Materials and methods

Chemicals

Chlorothalonil, 100 µg·mL	extsuperscript{−1} standard, (Ministry of Agriculture Environmental Protection Research Institute, Tianjin); n-Hexane (chromatographic purity >95%, Honeywell Trading Co., Ltd., Shanghai).

SPME extraction conditions optimization

In this experiment, the extraction head (A), the extraction temperature (B), the extraction time (C), the stirring rate (D), the NaCl concentration (E) and four levels were selected, using L16 (4	extsuperscript{5}) plus Cross-design (Table 1), SPME orthogonal experiments, analysis of variance, to determine the optimal SPME extraction conditions.

At room temperature, the apple samples purchased from the market were hit with a homogenizer. Weigh accurately 2.00 g of a 20 mL extraction bottles, and then added 0.50 mL standard solutions of four organochlorine (1.00 µg·mL	extsuperscript{−1}) and 0.10 mL NaCl solution. After mixing, a magnet (600 r·min	extsuperscript{−1}) was placed into the bottle, and the sample bottle cap was closed, the extraction head of the solid phase micro extractor inserted into the sample bottle, and pushed out the fiber head (was careful not to touch the liquid surface and bottle wall). Put it in a magnetic stirrer, then stirred and extracted at 50°C for 10 min. After adsorption, the fiber head was retracted, extraction head (SPME Fiber Assembly 65 um PDMS/DVB, Fused Silica 24 Ga, Manual Holder, 3pk; Supelco Co., Ltd., America) was removes from the sample bottle and quickly inserted the extraction head into the inlet of the gas chromatography mass spectrometer. The fiber tip was analyzed at the inlet 250°C for 5.00 min when the instrument turned on and data were collected.

Soils

Two different agricultural soils were selected for this study, SoilA (Urumqi, Xinjiang, clay); Soil B (Changji, Xinjiang, sand). All of 0–20 cm soil layers. Both soils were sieved through sieve of 2 mm.

The main characteristics of the soil organic matter were determined by potassium dichromate volumetric method according to NY/T 1121.6–2006; total nitrogen was determined by Kjeldahl method according to NY/T 1121.24–2012; pH was determined by potentiometry method according to LY/T 1239–1999; cation exchange capacity was determined by neutral ammonium acetate method according to LY/T 1243–1999; conductivity was determined by electrode method; particle-size composition was determined by hydrometer method according to LY/T 1225–1999.

Adsorption experiment

Chlorothalonil solutions were added separately to vials of 25 mL at a mass concentration of 0.5, 1, 5, 10 and 50 µg·mL	extsuperscript{−1}. 5.0 g soils through 0.25 mm sieve were added to each vial. The soil was shaken in a water bath at a constant temperature of (25 ± 2) °C for 24 h. The supernatant from each vial was transferred to a centrifuge tube and centrifuged at 10 000 r·min	extsuperscript{−1} for 10 min. The supernatant was placed in a solid-phase microsensor bottle and the concentration of the soil in the different types of soil to be measured. Each experiment was repeated three times.

Leaching experiment

Soil columns were made by PVC pipe (60 cm × 5 cm), both soils were over 2 mm sieve, and then were packed into soil columns, the quality of soil A and soil B was 960 g and 1300 g, respectively. In the upper and lower layers of the soil columns, 5 cm high pre-selected and cleaned quartz sands were placed on the top and bottom of the soil column, and two layers of gauze are placed on the top and bottom quartz sand to prevent soil particles loss. Finally, tap water was evenly penetrated into the soil column. Before the experiment, the soil in all soil columns was moistened with 0.01 mol·L	extsuperscript{−1} of CaCl	extsubscript{2} in room temperature (temperature about 20 degree Celsius, humidity about 30%). After running for 24 hours, after saturating the soil, chlorothalonil with various concentrations was added. After running for 24 hours, pesticides reached saturation in soil columns.

The concentration of chlorothalonil was selected as 75, 150, and 300 µg·mL	extsuperscript{−1}, which represent high, medium, and low concentrations, respectively.

| Table 1. Cross-design of SPME extraction condition. |
|---------------------------------|
| Level | A | B (°C) | C (min) | D (r·min	extsuperscript{−1}) | E (%) |
|-------|---|--------|--------|-----------------|------|
| 1     | 100 µm PDMS | 40 | 50 | 300 | 2 |
| 2     | 65 µm PDMS/DVB | 50 | 40 | 1200 | 5 |
| 3     | 50/30 µm DVB/CAR/PDMS | 60 | 30 | 1500 | 10 |
| 4     | 75 µm Carboxen/PDMS | 70 | 20 | 600 | 20 |
10 mL of chlorothalonil was added to the soil column (soil A and soil B) at three concentrations. After running for 24 hours in room temperature (temperature about 20 degrees Celsius, humidity about 30%), the pesticide and soil reached saturation, and the leaching was immediately started. Using continuous leaching, the tap water (flow rate was 30 mL·h⁻¹) was collected every 50 mL and the leachate was collected 10 times in total. Then, each leachate from each soil column was immediately placed in a 4°C refrigerator for storage and the content of chlorothalonil in the leachate of each part was determined. After the leaching was completed, the soil column was evenly divided into 0 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 50 cm (a total of 5 sections of soil columns). The content of chlorothalonil in the soil column of each part was determined. Each group was created with 3 groups in parallel.

**Degradation experiment**

Different textures of soil (soil A and soil B) were accurately weighed 20 g into 150 mL glass flasks. The chlorothalonil solution was added to each flask in an appropriate amount. Before the experiment began, the soils in all beakers were moistened with 0.01 mol·L⁻¹ of CaCl₂. After standing for 24 hours, after the soil is saturated, chlorothalonil solution with different concentrations are added to each glass flask. The concentration of chlorothalonil was 5, 20 and 50 mg·kg⁻¹, respectively. These three concentrations represented the three types of low, medium, and high concentrations, respectively. Sufficient Milli-Q water will be added to each flask to adjust the moisture content of soils, approximately 85% of the water holding capacity (FC) and the moisture content of soils were maintained by adding Milli-Q water every week in this experiment. And the quality of the water to be added can be known through the total mass of water and soil. Glass flasks were stored in a dark and confined space and the temperature in space was controlled at 25°C ± 2°C. The content of chlorothalonil in soil samples was determined after 0, 1, 3, 7, 14, 21, 28, 35, and 45 d.

**GC-MS analysis**

Chromatographic conditions: HP 5-MS capillary column (30 m × 0.25 mm × 0.25 μm). Temperature program: hold at 100°C for 2 min, rised to 150°C at a rate of 10°C·min⁻¹ and hold 2 min, then rised 192°C at a rate of 3°C·min⁻¹, finally, rised 252°C at a rate of 30°C·min⁻¹ and hold 2 min. Flow rate of He was 1.4 mL·min⁻¹. Inlet temperature was 250°C. Split ratio was 10:1. The ionic mass-to-charge ratio was selected as the qualitative and the peak area was selected as the quantitative.

Mass spectrometry conditions: ionization mode was EI, electron energy was 70 eV, the temperature of ion source was 230°C, the temperature of quadrupole was 150°C, temperature of transmission line was 250°C, C, solvent delays were 4 min.

**Data analysis**

The adsorption kinetics of chlorothalonil in different soils could be analyzed using public Freundlich model: 

\[ Q_e = K C_e^{1/n} \]

In the formula, \( Q_e \) was expressed as the mass fraction of chlorothalonil adsorbed on the soil (mg·g⁻¹); \( C_e \) was the concentration of solution of chlorothalonil in water (mg·L⁻¹) at the time of adsorption equilibrium, and \( K \) was the adsorption constant of model Freundlich (L·kg⁻¹), the greater the K value, the stronger the adsorption capacity of the soil to chlorothalonil pesticides.

The adsorption free energy (G) in soil could directly reflect the adsorption mechanism of chlorothalonil in soil. The adsorption model could be expressed by the following formula: 

\[ \Delta G = - R T \ln K_{OM} \]

In the formula, \( \Delta G \) was expressed as the magnitude of the change in soil adsorption free energy, \( R \) was expressed as the molar gas constant (8.314 J·K⁻¹·mol⁻¹), \( T \) was the absolute temperature, and \( K_{OM} \) was the organic matter in different soil.

Residue degradation dynamics could be represented by first-order kinetic model 

\[ C_t = C_0 e^{-kt} \]

\( C_t \) was the amount of residual chlorothalonil (mg·kg⁻¹) at t after application, and \( C_0 \) was the original amount of pesticide (mg·kg⁻¹), \( k \) was the degradation coefficient, t was the time (day) after application.

The calculations for all experiments were analysed using Excel, Origin 8.5, and Spss 20.0.

**Results and discussion**

**SPME orthogonal experiment optimization results**

**The result of orthogonal experiment**

Orthogonal experimental analysis showed (Table 2) that the factors affecting SPME extraction efficiency were A > E > B > D > C, and the optimal SPME extraction result was A₂B₂C₁D₁E₁, in other words, using a 65 μm PDMS/DVB extraction head, at 50°C, speed 600 r·min⁻¹, NaCl concentration 10% for 50 min. From the analysis of variance (Table 3), it could be seen that extraction head had most significant effect on the orthogonal experiment.

**Linear range, limit of quantification and detection limit of four organochlorine pesticides**

Under optimized experimental conditions, standard solutions of 0.02 to 2.00 μg·mL⁻¹ (Heptachlor...
quantification was 2.8 ~ 20.6 μg·kg$^{-1}$. The LOD of chlorothalonil was 0.8 μg·kg$^{-1}$, the linear range was 0.02 ~ 2.00 μg·kg$^{-1}$. Đurović-Đejić et al. (2019) studied three sample preparation methods for the simultaneous determination of 12 pesticides, which the LOD of chlorothalonil was 7 μg·kg$^{-1}$ using QuEChERS, 11 μg·kg$^{-1}$ by traditional solid-liquid extraction and Soxhlet extraction. The LOD of all three methods were higher than the optimized SPME method. And compared with the traditional solvent extraction method, the SPME preparation method required less solvent and was an environmentally friendly method.

**Recovery rate of four organochlorine**

The contents of the four organochlorine pesticide residues in the grape samples by this method were lower than the detection limit of this method, so the original residue of the grape samples were regarded as 0 mg·kg$^{-1}$. Add three levels concentration of 0.05 mg·kg$^{-1}$ (heptachlor, 0.08 mg·kg$^{-1}$, PCNB, 0.02 mg·kg$^{-1}$), and 1.5 mg·kg$^{-1}$ to the sample, respectively. Three parallel experiments were performed at each concentration. The results are shown in Table 5. Table 5 shows that the average recoveries of the four pesticides from 83.3% to 93.4%, and the relative standard deviations were 2.5% to 8.4%, which were constant with the requirements of pesticide residue analysis.

**The result of chlorothalonil in adsorption experiment of tested soils**

**Physical and chemical properties of tested soils**

Physical and chemical properties of tested soils are shown in Table 6. The organic matter and total nitrogen

### Table 2. Orthogonal experimental design and L16 (4$^5$) visual analysis table.

| NO | A | B | C | D | E | Recovery rate % |
|----|---|---|---|---|---|------------------|
| 1  | 1 | 1 | 1 | 1 | 1 | 25.780          |
| 2  | 1 | 2 | 2 | 2 | 2 | 32.620          |
| 3  | 1 | 3 | 3 | 3 | 3 | 19.190          |
| 4  | 1 | 4 | 4 | 4 | 4 | 8.520           |
| 5  | 2 | 1 | 2 | 3 | 4 | 22.700          |
| 6  | 2 | 2 | 1 | 4 | 3 | 95.480          |
| 7  | 2 | 3 | 4 | 1 | 2 | 55.130          |
| 8  | 2 | 4 | 3 | 2 | 1 | 58.810          |
| 9  | 3 | 1 | 3 | 4 | 2 | 14.160          |
| 10 | 3 | 2 | 4 | 1 | 3 | 11.910          |
| 11 | 3 | 3 | 1 | 2 | 4 | 14.720          |
| 12 | 3 | 4 | 2 | 1 | 3 | 1.940           |
| 13 | 4 | 1 | 4 | 2 | 3 | 2.680           |
| 14 | 4 | 2 | 3 | 1 | 4 | 1.940           |
| 15 | 4 | 3 | 2 | 4 | 1 | 1.940           |
| 16 | 4 | 4 | 1 | 3 | 2 | 1.980           |

### Table 3. Variance analysis table.

| Factor    | Sum of square deviation | Degree of freedom | F | F critical value | eminence |
|-----------|-------------------------|-------------------|---|-----------------|----------|
| A         | 7174.119                | 3                 | 3.521 | 3.290 | *         |
| B         | 740.967                 | 3                 | 0.364 | 3.290 |           |
| C         | 755.664                 | 3                 | 0.371 | 3.290 |           |
| D         | 589.486                 | 3                 | 0.338 | 3.290 |           |
| E         | 836.248                 | 3                 | 0.406 | 3.290 |           |
| deviation | 10,186,480              | 15                |       |                |          |

### Table 4. Linear ranges, linear equations, correlation coefficients, detection limits, and limits of quantification of four organochlorine pesticides.

| Analyte           | Linear range (μg·mL$^{-1}$) | Linear equation | $R^2$ | LOD (μg·kg$^{-1}$) | LOQ (μg·kg$^{-1}$) |
|-------------------|-----------------------------|-----------------|-------|-------------------|-------------------|
| Hexachlorobenzene | 0.02 ~ 2.00                 | $Y = 12936X-63.21$ | 0.9993 | 0.8              | 2.8              |
| PCNB              | 0.02 ~ 2.00                 | $Y = 3738X+12.58$ | 0.9992 | 2.1              | 6.9              |
| Chlorothalonil    | 0.02 ~ 2.00                 | $Y = 8601X-187.5$ | 0.9994 | 0.8              | 2.8              |
| Heptachlor        | 0.05 ~ 2.00                 | $Y = 1529X-24.33$ | 0.9965 | 6.2              | 20.6             |

### Table 5. The recovery and accuracy of four organochlorine pesticides in grape.

| Analyte           | Added amount (mg·kg$^{-1}$) | measured value (mg·kg$^{-1}$) | Recovery rate (%) | RSD % |
|-------------------|-----------------------------|-------------------------------|-------------------|-------|
| Hexachlorobenzene | 0.05                        | 0.046                         | 91.2              | 2.5   |
| PCNB              | 0.05                        | 0.461                         | 92.2              | 2.6   |
| Chlorothalonil    | 0.05                        | 0.904                         | 94.5              | 2.1   |
| Heptachlor        | 0.05                        | 0.423                         | 84.6              | 5.2   |

0.05 ~ 2.00 μg·mL$^{-1}$ different target analyses were formulated based on 10 μg·mL$^{-1}$ of mother liquor. A series of standard solutions in different concentrations were formulated and each concentration parallel experiment 3 times, the target analyzes standard curves were drawn with the target analyzes concentration (μg·mL$^{-1}$) as abscissa X, the peak area as ordinate Y. The correlation coefficients, detection limit, and limit of quantification were shown in Table 4. From the table, it could be seen that the linear ranges of Hexachlorobenzene, PCNB and Chlorothalonil were 0.02 ~ 2.00, and Heptachlor was 0.05 ~ 2.00. The peak area of the four organochlorine pesticides showed a good linear relationship with the corresponding concentration, the linear correlation coefficient of four organochlorine were greater than 0.9992, the detection limit was 0.8 ~ 6.2 μg·kg$^{-1}$, and the limit of
content of soil A were much higher than that of soil B, but the cation exchange capacity of soil A was much lower than that of soil B. In term of soil clay, the clay of soil A was slightly higher than soil B. The physical and chemical properties of the soil may affect the adsorption of pesticides in the soil, and then affect the degradation and leaching of pesticides in the soil (Garba et al., 2018; Huang et al., 2019).

**Absorption experiment of chlorothalonil in different soils**

The Freundlich adsorption model parameters and adsorption free energy change ΔG of chlorothalonil in the two soils are shown in Table 7. K values of Soil A and soil B were 6.7158 and 1.2568, respectively, indicating that soil A had a strong adsorption effect on chlorothalonil.

The free adsorption energy of the two soils was also different. The free adsorption energy of soil A was $-12.9568 \text{kJ} \cdot \text{mol}^{-1}$, and free adsorption energy of soil B was $-17.5219 \text{kJ} \cdot \text{mol}^{-1}$. The adsorption of the two soil was different. The free energy change was negative, and its absolute value was less than 40 kJ/mol. Therefore, it was known that chlorothalonil belonged to the physical adsorption in both soil and was spontaneous reversible adsorption process. So, soil did not lose its activity after chemical reactions with soil components. Yavari et al. (2019) believed the herbicides adsorptions were physical and spontaneous processes as ΔG values were negative and below 40 kJ/mol. There were also some other reports on the physical adsorption of pesticides have also been reported in some literatures (Garba et al., 2018; Wang et al., 2019).

**Effects of leaching water on leaching and transport of chlorothalonil in different soils**

The amount and depth of pesticide infiltration in different soils after rainfall and irrigation were the two main factors in assessing pesticide pollution to groundwater. Therefore, it was very important to study the content of chlorothalonil in the leachate and the soil after irrigation. In this paper, the content of leachate of chlorothalonil during rainfall and the residual amount of chlorothalonil in soil after rainfall were studied by simulated rainfall. The results of different leachate on the leaching of chlorothalonil in soil A and soil B were shown in Figure 1. And the results of Figure 1 indicated that under the three concentrations, with the increase of leachate, the content of chlorothalonil increased first and then decreased. But the content of chlorothalonil was slightly different in soil A and B.

For soil A, at three concentration, the content of chlorothalonil was highest when leachate was 250 mL, which was 0.0503, 0.4977 and 0.0550 μg·g⁻¹, respectively. The results of the leaching and transport of chlorothalonil in soil B are illustrated in Figure 1. Under the high concentration treatment, the content of chlorothalonil was the most highest when the volume of leachate was 250 mL, which is 0.0498 μg·g⁻¹. But at low and medium concentration, the content of chlorothalonil was the most highest when the volume of leaching water is 100 mL, which was 0.0082 and 0.0088 μg·g⁻¹. Under unusual concentrations of application, although the difference in the amount of application in the same soil affected the vertical distribution of chlorothalonil in the soil to a certain extent, did not significantly affect the leaching of chlorothalonil from the soil. The residual amount of chlorothalonil in the leachate was soil A> soil B, indicated that soil A was more than soil B in moving.

The residual amount of chlorothalonil in different soils column is shown in Figure 2. Under different concentrations, the residual amount of chlorothalonil in both soil column was concentrated in the 0 to 10 cm (topmost) section of soil, with the soil layer. As the depth increased, the amount of chlorothalonil residue in each soil column also decreased. Under the T3 (300 μg·mL⁻¹) treatment, the soil A and soil B at 0–10 cm were 10.6956 and 83.7931 μg·g⁻¹, respectively. The highest amount of residue in this treatment, but with the decline in the concentration, the residual amount gradually decreases. Therefore, under the three concentrations of treatment, the residual amount of chlorothalonil was soil A< soil B. In each leaching solution, the content of chlorothalonil in soil B was much lower than that in soil A. Combining Figure 1, a large amount of chlorothalonil remained in the soil and was not leached. It indicated that the migration of chlorothalonil in soil B was lower than that in soil A, and it belonged to not easy to migrate in sand soil. Therefore, chlorothalonil could easily

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**Table 6. Physical and chemical properties of tested soils.**

| Soil | OM (g·kg⁻¹) | Total nitrogen (g·kg⁻¹) | pH | CEC (cmol·kg⁻¹) | Conductivity (μS·cm⁻¹) | Clay (%) | Sand (%) | Silt (%) |
|------|-------------|-------------------------|----|-----------------|------------------------|---------|---------|---------|
| Soil A | 36.06 | 2.7 | 8.1 | 15.49 | 2.24 | 12.9568 | 54.31 |
| Soil B | 1.07 | 0.5 | 7.71 | 28.50 | 1.29 | 11.81 | 33.86 |

*OM: Organic matter.
*CEC: Cation exchange capacity.

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**Table 7. Parameters of Freundlich equation for chlorothalonil adsorption in soils.**

| Soil | R² | n | K | Kᵣ | ΔG (kJ·mol⁻¹) |
|------|----|---|---|----|--------------|
| Soil A | 0.9675 | 1.1637 | 6.7158 | 186.2404 | -12.9568 |
| Soil B | 0.9777 | 0.7256 | 1.2568 | 1174.5794 | -17.5219 |
contaminate underground water resources in soil A (clay). Dufilho (Dufilho & Falco, 2020) analyzed the leaching characteristics of chlorpyrifos in sand and clay, the result indicated the sandy loam texture soil produced more percolation of irrigation water, but the clay loam soil produced greater leaching of chlorpyrifos under similar application conditions, this was consistent with the findings of this study.

The degradation of chlorothalonil in different soil

The degradation kinetics of chlorothalonil in different soil was consistent with the first-order degradation kinetics equation (Table 8). With the increased of spray dose, the kinetic parameters of degradation of chlorothalonil were also changed. The degradation factor followed the spraying dose increased first and then decreased. The degradation rate of chlorothalonil in soil A was presented in Figure 3. In the different concentrations, chlorothalonil residues were the highest in 0 day after application, and then decrease as the effect time increased, and the degradation rate also increases. In 0 ~ 7 days, the degradation rate of chlorothalonil in soil A increased rapidly. After 7 days of application, the degradation rate gradually became flat, the degradation rate gradually became dull with increase of time, the higher the concentration of chlorothalonil, the slower the degradation, and the higher the final residual amount of chlorothalonil. Table 8 shows the first-order kinetic equation of chlorothalonil in different soil. The results demonstrated that the half-life was also prolonged with the concentration increase of chlorothalonil. As can be seen from Table 8, the degradation half-life of chlorothalonil was 9.79 d, 8.77 d and 12.83 d in T1, T2, T3, respectively.

The degradation rate of chlorothalonil in soil B is shown in Figure 3. It could be seen that in different concentrations, the degradation rate of chlorothalonil was significantly different. In T3, the degradation rate
of chlorothalonil continued to accelerate in 0–45 d, but at T1 and T2, the degradation rate of chlorothalonil was lower than T3. At T1 and T2, the degradation rate of chlorothalonil was faster at 0–28 d, but at 28–45 d, the degradation rate gradually became slower after application. Table 8 shows that the half-life of soil B in diverse application concentrations and the half-life was 15.07d, 23.90d, and 27.07d, respectively.

Table 8. Degradation first-order kinetic equation of chlorothalonil in different soils.

| soil  | Original residue (mg·g⁻¹) | T1               | T2               | T3               |
|-------|----------------------------|------------------|------------------|------------------|
| Soil A| 0.1336                     | 0.0358           | 0.1064           | 0.3889           |
| Kinetic equations | Cₜ = 0.0319e⁻⁰.⁷³₇₈ᵗ   | Cₜ = 0.108e⁻⁰.⁰⁷⁹ᵗ | Cₜ = 0.3318e⁻⁰.⁰⁵₆₀ᵗ |
| R²    | 0.9748                     | 0.9894           | 0.9655           |
| half life | 9.79                      | 8.77             | 12.83            |
| Soil B| 0.1336                     | 0.0348e⁻⁰.⁴₅₀₀ᵗ  | 0.2208e⁻⁰.₀₂₉₀ᵗ | 0.4976e⁻₀.₀₂₃₈ᵗ |
| Kinetic equations | Cₜ = 0.0348e⁻⁰.⁴₅₀₀ᵗ | Cₜ = 0.2208e⁻⁰.₀₂₉₀ᵗ | Cₜ = 0.4976e⁻₀.₀₂₃₈ᵗ |
| R²    | 0.9524                     | 0.9834           | 0.9527           |
| half life | 15.07                     | 23.97            | 27.07            |

With the increase of application concentration, the residual amount and half-life of chlorothalonil in different soil also increased. The degradation rate was: low concentration > medium concentration > high concentration, and the half-life time: Soil A < Soil B. The result may be because soils with high organic matter content contain various microorganisms, which is more conducive to the degradation of pesticides in the soil (Dai & Shelley, 2004; Ishag et al., 2016; H. Li et al., 2019; Singh et al., 2003; Y. Sun et al., 2019).

Correlation analysis of adsorption, leaching and degradation characteristics of chlorothalonil and soil physical and chemical properties

Correlations between residues and physical and chemical properties in soil A are shown Table 9. There was a significant correlation between pH and cation exchange capacity. According to the study of Jaime (Jaime et al., 2008), there is a negative correlation between pH and soil adsorption, indicating that the pH of the soil was indeed an important factor affecting soil leaching characteristics. The key factors for the content of pesticide residues in Qingling clay (soil B) were as showed in Table 10. There was a significant correlations among the four basic physicochemical properties of aggregate nitrogen, cation exchange capacity, pH value, and granular mechanical composition in soil B, indicating that these four physical and chemical properties were affected.

Table 9. Correlations between residues and physical and chemical properties in soil A.

| Residues | OM | Total nitrogen | pH | CEC | Conductivity | clay | sand | silt |
|----------|----|----------------|----|-----|--------------|------|------|------|
| Residues | 1  | 0.041          | 1  | 0.421 | 0.923        | 1    |      |      |
| OM       | 0.421 | 0.923         | 1  |       |              |      |      |      |
| Total nitrogen | 0.421 | 0.923         | 1  |       |              |      |      |      |
| pH       | -0.912 | -0.447        | -0.756 | 1    |              |      |      |      |
| CEC      | -0.897 | -0.498        | -0.792 | 0.998* | 1            |      |      |      |
| Conductivity | 0.179 | -0.976        | -0.817 | 0.24 | 0.296        | 1    |      |      |
| clay     | 0.506 | -0.841        | -0.569 | -0.108 | -0.05        | 0.939 | 1    |      |
| sand     | 0.995 | -0.06         | 0.327 | -0.666 | -0.836        | 0.277 | 0.59 | 1    |
| silt     | -0.719 | 0.665         | 0.327 | 0.371 | 0.317        | -0.812 | -0.963 | -0.786 |
According to Tables 9 and 10, it can be seen that the factors affecting the adsorption, leaching, and degradation characteristics of chlorothalonil in the two soils are slightly different, which may be caused by the very different physical and chemical properties of soil A (clay soil) and soil B (sandy soil).

There was literature indicated that OM and clay content were found to be important in determining adsorption, pH is negatively correlated with adsorption (Jaime et al., 2008). From Table 7, The adsorption capacity of soil A to chlorothalonil was higher than that of soil B. The OM, pH, and clay content of soil A were higher than those of soil B. The results were consistent with the literature.

Degradation rate was positively correlated with OM and clay content, and negatively correlated with pH (Jaime et al., 2008). From Figure 3 and Table 8, it was shown that the degradation rate of soil A was higher than that of soil B. And the OM, pH, and clay content of soil A were higher than those of soil B. The results were consistent with the literature.

Table 10. Correlations between residues and physical and chemical properties in soil B.

| Residues | OM     | Total nitrogen | pH     | CEC     | Conductivity | clay     | sand | silt    |
|----------|--------|----------------|--------|---------|--------------|----------|------|---------|
|          |        |                |        |         |              |          |      |         |
| Residues | 1      |                |        |         |              |          |      |         |
| OM       | −0.897 | 1              |        |         |              |          |      |         |
| Total nitrogen | −0.998* | 0.923  | 1      |         |              |          |      |         |
| pH       | 0.797  | −0.447         | −0.756 | 1       |              |          |      |         |
| CEC      | 0.83   | −0.498         | −0.792 | 0.998*  | 1            |          |      |         |
| Conductivity | 0.778  | −0.976         | −0.817 | 0.24    | 0.296        | 1        |      |         |
| clay     | 0.968  | −0.979         | −0.982 | 0.619   | 0.663        | 0.911    | 1    | 0.5     |
| sand     | −0.702 | 0.315          | 0.655  | −0.99   | −0.98        | −0.099   | −0.5 | 1       |
| silt     | −0.668 | 0.27           | 0.619  | −0.982  | −0.969       | −0.052   | −0.459 | 0.999* |

Conclusions

Chlorothalonil (CTN) was a broad-spectrum fungicide widely used in the control of downy mildew, anthracnose, and diseases in various crops, such as fruit and vegetables, cereals, etc. When chlorothalonil acted on crops, part of chlorothalonil acted on the crops and part of it went into the soil. By studying the adsorption, leaching and degradation characteristics of chlorothalonil in clay (soil A) and sand (soil B), the harm of chlorothalonil to soil and groundwater is understood.

It could be known from the optimization of the conditions that the optimal extraction condition of chlorothalonil was using 65 μm PDMS/DVB extraction head, and the extraction was maintained for 50 minutes under the conditions of 50°C, 600 r·min⁻¹ of rotating speed, and NaCl concentration of 10%.

The experiment resulted in the following conclusions: the adsorption experiments of different concentrations of chlorothalonil in two kinds of soils, it can be seen from the change of the free energy of adsorption that both kinds of soils belong to physical adsorption. From Freundlich adsorption model parameters, it is known that both kinds of soils were difficult to adsorb.

It can be known from the leaching experiment that under different application concentrations, the residual amount of chlorothalonil in the leachate was soil A > soil B. And under the three concentrations of treatment, the residual amount of chlorothalonil was: soil A < soil B. It could be known from the content of chlorothalonil in soil and leachate that chlorothalonil was more likely to migrate in clay (soil A) and therefore more likely to cause groundwater pollution. It could be seen that chlorothalonil was more suitable for use in sandy land. Under the T3 (300 μg·mL⁻¹) treatment, the soil A and soil B at 0–10 cm of soil column were 10.6956 and 83.7931 μg·g⁻¹, respectively. The highest amount of residue in this treatment, but with the decline in the concentration, the residual amount gradually decreases. Therefore, it was necessary to pay attention to the use concentration when applying the drug, and try to reduce the use concentration under the effect of chlorothalonil.

The degradation kinetics of both soil met the first-order kinetic equation. The amount and half-life of CTN increased with the increased in application concentration. The degradation rate was in three concentrations: T1 > T2 > T3. The half-life time was: T3 > T2 > T1 (T1, T2, T3 was 5, 20, 50 mg·kg⁻¹, respectively), half-life of soil A was less than soil B, indicating that chlorothalonil was more easily degraded in soil A than soil B. Combined with leaching experiments, it can be seen that chlorothalonil is easier to migrate and degrade in clay (soil A).

The pH value, total nitrogen, electrical conductivity, and organic matter in the soil were the key factors affecting the chlorothalonil residue content. From the correlations between residues of CTN and physical and chemical properties of the soil A and soil B, it showed that the content of OM and clay were
positively correlated with the adsorption of chlorothalonil in the soil, and negatively correlated with the pH value. It also showed that the content of OM and clay and pH value were positively correlated with degradation rate. Therefore, it could be known that the soil with high OM content was more conducive to the degradation of chlorothalonil.

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No potential conflict of interest was reported by the authors.

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