

RESEARCH ARTICLE

Dissipation of tiafenacil in five types of citrus orchard soils using the HPLC-MS coupled with the quick, easy, cheap, effective, rugged, and safe method

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Tiafenacil is a new contact herbicide and its environmental behavior after field application remains poorly understood. In order to understand the dissipation of tiafenacil in the soil, the tiafenacil dissipation experiment was conducted at citrus orchard sites in five provinces of China (Gansu, Shandong, Sichuan, Jiangxi, and Hainan) in 2019 and 2020 (July–August) and the relevant determination methods were optimized. The results showed that the established method showed good linearity in the concentration range of 0.01–0.5 mg/kg. The average recoveries of tiafenacil from the five soils were 86.31–101.66%, with coefficients of variation of 0.28–10.79%. The dissipation of tiafenacil at the five experimental sites conformed to the first-order kinetic equation, $C_t = C_0 \exp^{-kt}$ ($R^2 = 0.8130 - 0.9967$). The half-life of tiafenacil ranged from 0.26 to 4.19 days. The dissipation rate of tiafenacil was positively correlated with soil organic matter content and negatively correlated with soil pH, while monthly average temperature and total rainfall were less influential than soil properties. Therefore, the established method was simple and effective for tiafenacil residue analysis in citrus orchard soils. Tiafenacil could readily dissipate in soil and might be a safe alternative to glyphosate for weed control in citrus orchards.

KEYWORDS

dissipation kinetics, herbicides, high-performance liquid chromatography, orchard soil, tiafenacil

1 | INTRODUCTION

Since their emergence, chemical pesticides have played a vital role in improving the quality of agricultural products and promoting increased crop production and farmer income. Pesticide use not only improves living standards but also contributes to societal development [1–3]. However, pesticide residue retention in the environment is an

inevitable problem resulting from widespread pesticide application. Remaining applied pesticides not absorbed by crops or weeds will enter the soil and water, causing environmental pollution and endangering the ecosystem and human health [4, 5]. Therefore, studying the dissipation behavior of pesticides in the soil environment is important.

Soil contains complex organic and inorganic compounds, and its physicochemical properties can cause substantial interference when analyzing low-concentration pesticides [6]. Therefore, developing a suitable sample preparation method is key to successful determination

Article Related Abbreviations: CV, coefficient of variation; ME, matrix effect; PSA, *N*-propyl ethylenediamine

of pesticide dissipation. Conventional sample preparation methods, such as Soxhlet extraction [7] and liquid–liquid extraction [8], are considered to be time consuming and labor intensive, with excessive use of organic solvents, which can cause environmental pollution [9]. Owing to their shortcomings, conventional methods are gradually being replaced with simpler, faster, and more efficient sample preparation techniques, such as SPE, solid-phase microextraction, gel permeation chromatography, matrix solid-phase dispersion extraction, and the QuEChERS technique [10]. In particular, the QuEChERS technique, which became an international official method of the Association of Official Analytical Chemists in 2007 [11], has been widely used to analyze pesticide residues in soil [12].

Tiafenacil (CAS No. 1220411-29-9) is a new contact uracil-based herbicide developed by Farm Hannong (South Korea). Tiafenacil mainly controls monocotyledons, dicotyledons, and glyphosate-resistant weeds [13], and is considered an alternative to glyphosate and paraquat [14]. Regarding the mechanism of action, tiafenacil inhibits the formation of protoporphyrinogen oxidase during chlorophyll synthesis, resulting in the accumulation of photosensitive protoporphyrinogen IX, while singlet oxygen generated causes lipid peroxidation, which leads to the loss of cell membrane function and, therefore, growth suppression or even plant death [15]. As a protoporphyrinogen oxidase inhibitor, tiafenacil is characterized by a low dosage, high specificity in plants, and low toxicity in animals, shows no irritation of human skin and eyes, and does not readily accumulate in the environment [16]. Since its emergence in South Korea in 2018, researchers have investigated tiafenacil in terms of its mechanism of action [13], synthetic process [17], and food safety [18]. Currently, the environmental behavior of this herbicide after field application remains poorly understood.

Citrus (*Citrus reticulata* Blanco) is an important fruit tree species cultivated in China for more than 4000 years, and has a large market and diverse varieties. The citrus yield in China has been ranked as the highest in the world, while the trade volume is ranked third globally [19]. However, many species of weed, such as *Eleusine indica* (L.) Gaertn. and *Conyza canadensis* (L.) Cronq., grow rapidly and last for long periods in citrus orchards. Such weeds can cause serious harm to the yield and quality of citrus fruit, making it less competitive in the international market [20]. Glyphosate is still the main chemical herbicide used to control weeds in orchards. Owing to long-term use of the same herbicide, glyphosate-resistant weeds are continually emerging in various countries [21], with alternative herbicides urgently needed accordingly.

Based on a preliminary experiment in citrus orchards, we found that tiafenacil exhibited a positive effect on grass species, such as *E. indica* and *Setaria viridis* (L.) Beauv.,

and broadleaf species, such as *C. canadensis* and *Ambrosia artemisiifolia* L. Tiafenacil showed good control effect on all weeds and appeared to be safe for citrus trees. In the present study, we optimized the QuEChERS sample preparation technique and HPLC-MS to establish a method suitable for the rapid determination of tiafenacil residues in citrus orchard soil. We then analyzed the dissipation dynamics of tiafenacil residues in five different types of citrus orchard soils to provide evidence supporting the application of tiafenacil in citrus orchards.

2 | MATERIALS AND METHODS

2.1 | Reagents and standard solutions

Tiafenacil standard (purity $\geq 98\%$) and 5% tiafenacil suspension concentrate were provided by Farm Hannong (South Korea). Acetonitrile (UPLC/LC-MS grade) was purchased from Anpu Experimental Technology (Shanghai, China). Methanol, acetone, ethyl acetate, ammonia, dichloromethane, and NaCl (all of HPLC grade) were purchased from Xilong Science (Guangdong, China). Formic acid (88%, HPLC grade) was obtained from Comeo Chemical Reagents (Tianjin, China). Anhydrous $MgSO_4$ (analytical purity) was obtained from Daqing Chemical Pharmaceutical Factory (Tianjin, China). Octadecyl-bonded silica gel (C18; 50 μm , 60A) and *N*-propyl ethylenediamine (PSA; 40–63 μm , 60A) were manufactured by Agela Technologies (Shanghai, China). Ultrapure water was produced using a Milli-Q Advantage AW water purification system (Millipore, USA).

A sample of the tiafenacil standard (0.0102 g, accurate to 0.001 g) was accurately weighed using an electronic analytical balance (EX224ZH1/10000; Ohaus Instruments, Changzhou), China) and dissolved in acetonitrile to form a stock solution (1000 mg/L), which was stored in a refrigerator. Before experiments, an appropriate amount of the stock solution was diluted with acetonitrile to prepare a working solution (100 mg/L), which was stored in the dark at 4°C before use. The standard working solution was diluted to different mass concentrations and the standard curve was drawn according to experimental requirements.

2.2 | Experimental soils

Different types of citrus orchards soils were obtained from five regions in China. The soil types collected were red soil (Nanchang, Jiangxi Province), loessial soil (Maying, Gansu Province), brown soil (Jining, Shandong Province), purple soil (Chengdu, Sichuan Province), and latosol soil (Haikou, Hainan Province). Random soil samples were taken from a depth of 0–10 cm at experimental sites with

TABLE 1 Characteristics of citrus orchard soils and climatic conditions during the experiment (July–August) in 2019 and 2020

Year	Location	Soil	Classification ^a	Geographical coordinates	pH ^b	Organic matter ^c (g/kg)	Monthly average temperature ^d (°C)	Total rainfall ^d (mm)
2019	Gansu	Loessial soil	Cambisols	105°1' E, 35°18' N	8.15	0.83	19	115
	Shandong	Brown soil	Alisols	116°50' E, 35°37' N	5.70	7.23	25	428
	Sichuan	Purple soil	Gleysols	105°51' E, 30°56' N	7.60	0.46	26	633
	Jiangxi	Red soil	Ferralsols	115°36' E, 28°46' N	5.05	3.50	31	372
	Hainan	Latosol	Plinthosols	110°10' E, 19°32' N	5.78	3.92	30	528
2020	Gansu	Loessial soil	Cambisols	105°1' E, 35°18' N	8.13	0.75	21	249
	Shandong	Brown soil	Alisols	116°50' E, 35°37' N	5.81	7.71	26	504
	Sichuan	Purple soil	Gleysols	105°51' E, 30°56' N	7.85	0.66	25	675
	Jiangxi	Red soil	Ferralsols	115°36' E, 28°46' N	5.20	3.13	29	540
	Hainan	Latosol	Plinthosols	110°10' E, 19°32' N	5.75	4.80	29	654

^aWorld Reference Base for Soil Resources (WRB,1998).

^bSoil pH was determined with a water/soil ratio of 2.5:1 [22].

^cSoil organic matter content was determined using an elemental analyzer (vario MACRO cube, Elementar, Germany).

^dData from the China Weather Network (<http://www.weather.com.cn/cityintro/101240101.shtml>).

no history of pesticide application. After air-drying and the removal of debris, seeds, and plant roots, each sample was passed through a 20-mesh sieve (0.9 mm), then mixed evenly and packed into a sealed bag. The samples were stored in a freezer at -20°C before use. The major physiochemical properties of the experimental soils and the climatic conditions at the experimental sites are shown in Table 1 [22].

2.3 | Analytical methods

2.3.1 | Sample extraction and purification

A soil sample (5.0 g) was weighed into a 50-mL centrifuge tube, followed by the addition of ultrapure water (5 mL). The mixture was left to stand at room temperature for 0.5 h to allow the water to fully soak into the soil. Acetonitrile (10 mL) was then added to the centrifuge tube and the mixture was vortexed for 2 min using a vortex mixer (XW-18DL; Qiwei Instrument, Hangzhou, China). Next, NaCl (1.0 g) and MgSO_4 (1.0 g) were added to the centrifuge tube and the mixture was vortexed for 1 min until the aqueous phase gradually became clear. The tube was then centrifuged at 6,000 rpm ($4950 \times g$) for 5 min using a desktop refrigerated centrifuge (Digicen 21 R; Wiggens, Germany). Thereafter, the upper organic phase (1.5 mL) was transferred to a 2-mL centrifuge tube containing C18 (50 mg) and MgSO_4 (150 mg) for purification. After vortexing for 1 min, the supernatant was centrifuged at 4000 rpm ($2200 \times g$) for 5 min. The supernatant was filtered through a $0.22 \mu\text{m}$ organic filter membrane and analyzed by HPLC-MS.

2.3.2 | HPLC-MS analysis

The tiafenacil concentration in the extracts was analyzed using an Agilent 1260 Series high-performance liquid chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with an automatic injection device and a Zorbax Eclipse XDB-C18 column ($4.6 \text{ mm} \times 150 \text{ mm}$, $5 \mu\text{m}$; Agilent Technologies), and coupled with an Agilent 6120 Series single-stage four-bar mass spectrometer (Agilent Technologies). The major HPLC-MS parameters were as follows: Sample volume, $10 \mu\text{L}$; mobile phase, acetonitrile/0.1% formic acid solution 50:50, v/v; left and right column temperatures, 40°C ; velocity, 1 mL/min ; ESI ion source, positive ion scanning mode (ESI⁺); residence, 590 ms; relative residence, 100.0%; collision-induced dissociation voltage, 170 V; gain, 10.00; mass-charge ratio (m/z) of SIM mode, 534.1; capillary voltage, $\pm 3,000 \text{ V}$; drying temperature, 350°C ; dry gas flow rate, 12.0 L/min ; atomization pressure, 35 psig. Under these conditions, the retention time of each sample was approximately 5 min.

2.3.3 | Method validation

Pure acetonitrile and blank matrix solutions obtained after sample preparation were used to prepare standard working solutions with five different tiafenacil concentrations (0.01, 0.05, 0.1, 0.5, and 1 mg/L). The mass concentration of tiafenacil was taken as the abscissa (x), and the chromatographic peak area corresponding to each concentration was used as the ordinate (y) to draw the calibration curve. The linear regression equation and coefficient of determination (R^2) were obtained using Origin 2018 software

(OriginLab Corp., Northampton, MA, USA). The S/N was obtained at the lowest concentration of 0.01 mg/L, and the LOD and LOQ of tiafenacil were estimated using $S/N = 3$ and $S/N = 10$, respectively. Tiafenacil standard solutions of 0.01, 0.1, and 0.5 mg/kg were added to the blank soil samples for the recovery test. The spiked samples were recovered five times, nonspiked samples were used as blank controls, and the corresponding recovery and coefficient of variation (CV) were calculated.

The external standard method was applied to calculate the concentration of tiafenacil residues using the following equation [23]:

$$R (\%) = \frac{S_2 - S_0}{S_1} \times 100\% \quad (1)$$

where R is the tiafenacil recovery rate (%), S_2 and S_1 are the chromatographic peak areas of tiafenacil in soil samples and standard samples with the same tiafenacil concentration, respectively, and S_0 is the chromatographic peak area of the blank soil matrix without tiafenacil.

The matrix effect was calculated using the following equation [24]:

$$ME (\%) = \left(\frac{B}{A} - 1 \right) \times 100\% \quad (2)$$

where ME is the matrix effect, and A and B are the slopes of linear regression equation for tiafenacil concentration in the standard solution and blank matrix solution, respectively.

2.4 | Field experiment

The field experiment was conducted from July to August in 2019 and 2020 in citrus-growing areas of Gansu, Shandong, Sichuan, Jiangxi, and Hainan provinces in China. At each location, a 667 m² area of citrus orchard was used for the experiment. The citrus trees were 10 years old, and the average area of each tree was 10 m². Tiafenacil had not been applied previously and no weed control was conducted at the orchard sites. The experiment was conducted in accordance with the “Standard Operating Procedures for Field Efficacy Testing of Pesticide Residues” edited by the Ministry of Agriculture of the People’s Republic of China, and the newly revised Agricultural Industry Standard of the People’s Republic of China – “Guidelines for the Testing of Pesticide Residues in Crops: NY/T 788–2018”. Three doses of 5% tiafenacil suspension concentrate were applied, with active gradients of 0 g a.i./hm² (control), 160.50 g a.i./hm² (maximum recommended dose), and 240.75 g a.i./hm² (1.5 times the maximum recommended dose). Each exper-

imental plot was 40 m² in area, and each treatment was repeated three times. Tiafenacil was applied to the stems and leaves of citrus trees once using an SX-MD16E-2 backpack electric sprayer (Zhejiang Power Sprayer, China). Surface soil samples were collected 2 h, and 1, 2, 3, 5, 7, 14, 21, 30, and 45 days after application. In each plot, samples were collected at five to ten random points. After removing stones and other debris, samples from the same location were mixed and a subsample was taken using the quartering method. The samples were stored at –20°C before use.

2.5 | Kinetics analysis

A first-order kinetic model was adopted to simply describe the dissipation process of tiafenacil in the soil environment using IBM SPSS v25.0 software (IBM, Armonk, NY, USA). The dissipation kinetic parameters of tiafenacil dissipation were obtained using the nonlinear fitting method according to the following equation [25]:

$$C_t = C_0 \exp^{-kt}; \quad t_{0.5} = \frac{\ln 2}{k} \quad (3)$$

where C_t is the tiafenacil residue concentration (mg/kg), C_0 is the initial tiafenacil concentration after application (mg/kg), k and t are the dissipation coefficient (day^{–1}) and time after application (day), respectively, and $t_{0.5}$ (half-life) is the time required to degrade half of the tiafenacil applied.

3 | RESULTS AND DISCUSSION

3.1 | Optimization of the quick, easy, cheap, effective, rugged, and safe technique

3.1.1 | Optimization of sample extraction conditions

First, Association of Official Analytical Chemists Official Method 2007.01 (QuEChERS) was used to optimize the sample extraction procedure. Red soil from Jiangxi Province was spiked with tiafenacil at 0.1 mg/kg, with three replicates conducted simultaneously. The extraction efficiencies of acetonitrile, dichloromethane, methanol, ethyl acetate, and acetone as solvents were compared. The peak shapes of samples extracted by dichloromethane and ethyl acetate were poor, with many miscellaneous peaks. In contrast, samples extracted by acetonitrile, methanol, and acetone showed a smooth and good peak shape (Figure 1). Acetonitrile extraction resulted in the highest tiafenacil

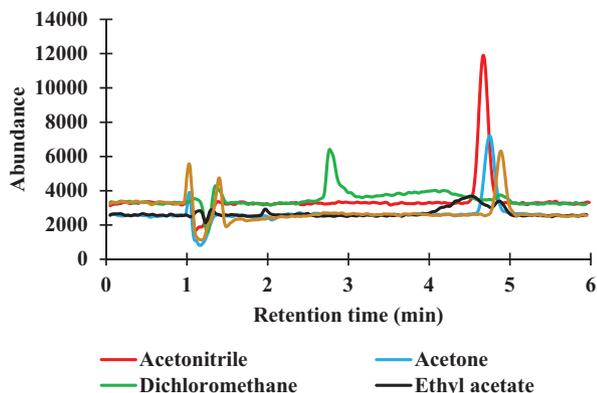


FIGURE 1 Effects of different extractants on the chromatographic peak shape of tiafenacil (0.1 mg/kg)

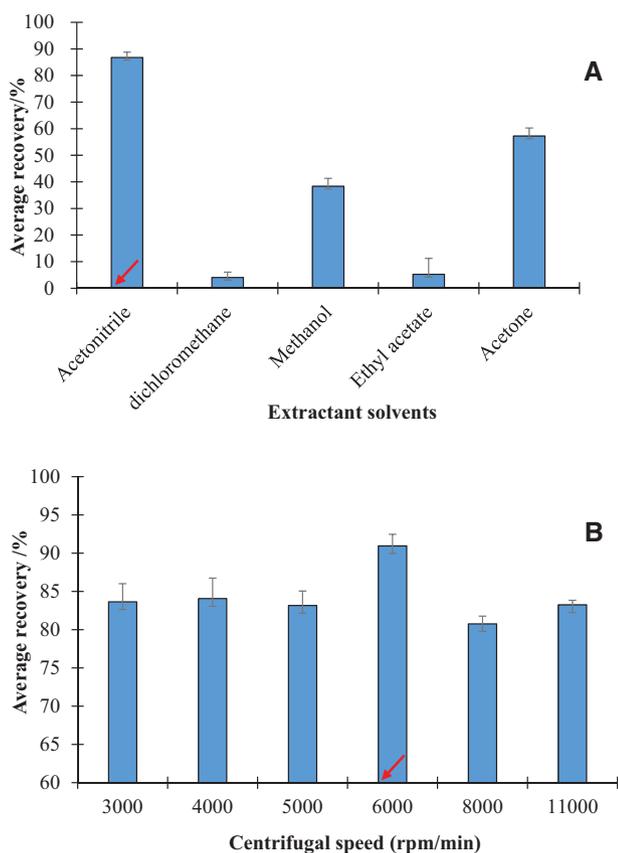


FIGURE 2 Recovery rate of tiafenacil from the red soil in Jiangxi Province using different extraction solvents (A) and centrifugal speeds (B) (spiked level = 0.1 mg/kg, $n = 3$)

recovery rate among the five solvents used (Figure 2A). Therefore, acetonitrile was selected as the extraction solvent for subsequent residue analysis.

To further optimize the extraction procedure, the effect of pH value on the extraction efficiency of acetonitrile was investigated. At three spiked levels of tiafenacil (0.01, 0.1, and 0.5 mg/kg), acetonitrile, 1% ammonia–acetonitrile, and 1% formic acid–acetonitrile were used as extraction

TABLE 2 Tiafenacil recovery rate obtained with different extractants

Spiked level (mg/kg)	Extractant	Average recovery (%)	RSD (%)
0.01	1% Ammonia–acetonitrile	96.96	8.64
	Acetonitrile	93.33	2.74
	1% Formic acid–acetonitrile	93.89	7.82
0.1	1% Ammonia–acetonitrile	88.25	0.66
	Acetonitrile	87.79	0.76
	1% Formic acid–acetonitrile	89.23	0.45
0.5	1% Ammonia–acetonitrile	95.62	1.28
	Acetonitrile	97.15	0.65
	1% Formic acid–acetonitrile	96.31	2.52

solvents. The resulting tiafenacil recovery rates were 87.79–97.15, 88.25–96.96, and 89.23–96.31%, respectively, indicating that different pH values had no significant effect on the extraction efficiency of acetonitrile (Table 2). Owing to its simple operation and low cost, pure acetonitrile was selected as the optimal solvent for sample extraction.

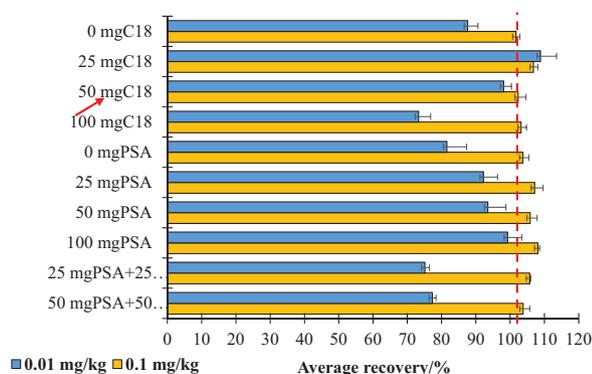
In the QuEChERS extraction procedure, salt is added to remove water and separate the organic and aqueous phases. Therefore, the salt content in the extraction procedure was optimized. Four combinations of salts (0.5 g NaCl + 1 g MgSO₄, 0.5 g NaCl + 2 g MgSO₄, 1 g NaCl + 1 g MgSO₄, and 1 g NaCl + 2 g MgSO₄) were applied to the three spiked levels of tiafenacil. The obtained tiafenacil recovery rates were 80.05–88.58, 80.94–94.70, 89.54–102.57, and 87.99–96.09%, respectively (Table 3). Therefore, 1 g each of NaCl and MgSO₄ was selected as the optimal added salt content. Furthermore, the effect of centrifugal force on the extraction procedure was examined at a spiked level of 0.1 mg/kg (Figure 2B). In the range of 3000–11 000 rpm (1238–16 639 × g), the highest tiafenacil recovery rate was obtained at 6000 rpm (4950 × g) under the selected extraction conditions. Based on these results, the optimal sample extraction conditions were obtained (as described in Section 2.3.1).

3.1.2 | Optimization of sample purification conditions

To eliminate the effects of impurities, such as organic matter in the soil, on herbicide residue analysis, the sample requires appropriate purification. C18 and PSA are commonly used as purification materials for soil matrices [26–28]. Herein, MgSO₄ (150 mg) was combined with different amounts of C18 (0–100 mg), PSA (0–100 mg), and their combinations (25 mg PSA + 25 mg C18, 50 mg PSA

TABLE 3 Effects of different salts on tiafenacil recovery rate at three spiked levels

Salt	Average recovery (%)		Average recovery (%)		Average recovery (%)	
	0.1 mg/kg	RSD (%)	0.1 mg/kg	RSD (%)	0.5 mg/kg	RSD (%)
0.5 g NaCl + 1 g MgSO ₄	80.05	5.95	86.11	3.60	88.58	3.39
0.5 g NaCl + 2 g MgSO ₄	80.94	5.52	91.51	3.16	94.70	3.12
1 g NaCl + 1 g MgSO ₄	89.54	9.86	98.22	5.19	102.57	0.37
1 g NaCl + 2 g MgSO ₄	87.99	7.62	95.61	4.81	96.09	0.46

FIGURE 3 Effects of different purification adsorbents on the recovery rate of tiafenacil from the red soil in Jiangxi Province (spiked level = 0.01 and 0.1 mg/kg, $n = 3$)

+ 50 mg C18) to purify soil samples spiked with 0.01 and 0.1 mg/kg of tiafenacil (using three replicates). The results of tiafenacil recovery test showed that the herbicide was recovered at rates of 73.30–108.87% (Figure 3). When the C18 dosage was 50 mg, the tiafenacil recovery rate at the two spiked levels was close to 100% (as indicated by the red dotted line in Figure 3). The purification effect of PSA at a dosage of 100 mg was similar to that obtained by 50 mg of C18. By accounting for cost and resource use, 150 mg MgSO₄ + 50 mg C18 was selected as the optimal combination of purification adsorbents.

3.2 | Optimization of HPLC-MS conditions

The HPLC-MS conditions were optimized using the tiafenacil standard solution at 0.1 mg/L. First, the chromatographic separation efficiencies of three mobile phases, acetonitrile–water, acetonitrile–0.1% formic acid solution, and methanol–water, were compared. The results showed a shorter retention time and better peak shape when acetonitrile–0.1% formic acid was used as the mobile phase. Therefore, the volume ratio of acetonitrile and 0.1% formic acid was optimized, with the optimal ratio determined to be 50:50 (v/v). Under the same chromatographic conditions, the standard sample was scanned in ESI^(+/-) mode in the range of m/z 100–1000, with

the strongest effective peak obtained in ESI⁺ mode at m/z 534.1. The parameters, including collision-induced dissociation voltage, were then optimized in SIM mode and optimal analytical conditions were obtained (as described in Section 2.3.2). Chromatograms of the standard solution and soil sample acquired under optimal HPLC-MS conditions are shown in Figure 4. The blank soil matrix and blank acetonitrile solvent showed very low responses at the same retention time as the spiked sample, not exceeding 20% of the LOQ at the spiked level. This result indicated that the optimized HPLC-MS method had good specificity for detecting tiafenacil residues in soil.

3.3 | Linearity, LOD, LOQ, and matrix effect of optimized method

Within the concentration range of 0.01–1 mg/L, a good linear relationship was observed between the mass concentration in solutions and peak area of tiafenacil ($R^2 > 0.999$). The sensitivity of the proposed method was also good. The LOD and LOQ of the method for tiafenacil in the five matrix solutions were estimated to be 2.6–3.1 $\mu\text{g}/\text{kg}$ and 8.8–10.3 $\mu\text{g}/\text{kg}$, respectively (Table 4). The LOQ of the method was selected to be 0.01 mg/kg.

In complex sample matrices, the matrix effect affects the analyte ionization efficiency, which in turn influences method accuracy and sensitivity [29]. When $|\text{ME}| < 20\%$, the matrix effect can be ignored, and when $|\text{ME}| \geq 20\%$, the matrix effect can enhance or reduce the analyte signal, with such an effect requiring elimination [30–32]. In this study, the $|\text{ME}|$ values did not exceed 10% in the five different soil matrices (Table 4), indicating no evident matrix effect of the soil samples, and that the purification effect was satisfactory.

3.4 | Method precision and accuracy

The accuracy and precision of the proposed method were evaluated using the recovery rate of spiked samples and the CV of multiple tests. When the recovery is 70–110% and $\text{CV} < 15\%$, the method is feasible. The average recoveries of tiafenacil from the five different soils ranged from 86.31%

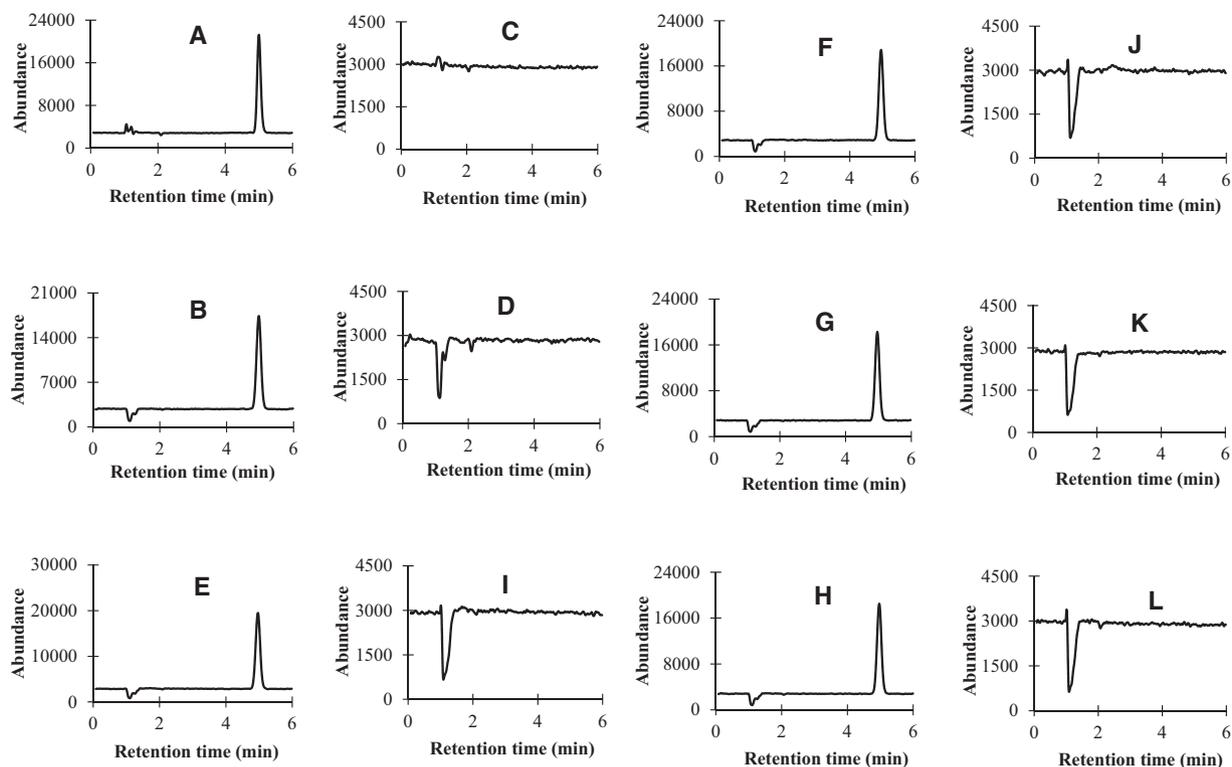


FIGURE 4 Chromatograms acquired under the optimized conditions. (a) Tiafenacil standard solution; (b) tiafenacil-spiked red soil; (c) blank acetonitrile solvent; (d) blank red soil matrix; (e) tiafenacil-spiked loessial soil; (f) Tiafenacil-spiked brown soil; (g) tiafenacil-spiked purple soil; (h) tiafenacil-spiked latosol; (i) blank loessial soil matrix; (j) blank brown soil matrix; (k) blank purple soil matrix; (l) blank latosol matrix. (spiked level = 0.1 mg/kg)

TABLE 4 Linearity, coefficient of determination (R^2), LOD, LOQ, and matrix effect of the established method for detection of tiafenacil in different matrices

Matrix	Linear equation	R^2	LOD ($\mu\text{g}/\text{kg}$)	LOQ ($\mu\text{g}/\text{kg}$)	Matrix effect (%)
Acetonitrile	$y = 1332756.1490x + 5863.6071$	0.9998	–	–	–
Loessial soil	$y = 1217591.4500x - 6713.6729$	0.9998	3.0	9.6	–8.64
Brown soil	$y = 1410043.8994x + 9494.3962$	0.9993	2.9	9.7	5.80
Purple soil	$y = 1460937.0688x + 4667.5235$	0.9999	2.6	8.8	9.62
Red soil	$y = 1319309.7925x + 9997.2241$	0.9993	2.8	9.0	–1.01
Latosol	$y = 1426326.0299x + 4850.5067$	0.9999	3.1	10.3	7.02

to 101.66%, with standard deviations of 0.25–9.31. The CVs ranged from 0.28 to 10.79% (Table 5). These variable values satisfied the requirements for pesticide residue analysis, indicating that the established method was accurate and precise, and, therefore, suitable for detecting tiafenacil residues in actual soil samples from citrus orchards.

3.5 | Dissipation of tiafenacil

The dissipation of pesticide residues in the field is a dynamic process affected by multiple environmental

factors [33]. In this study, the dissipation dynamics of tiafenacil in different citrus orchard soils were described by the first-order kinetic equation, and the dissipation level of tiafenacil was expressed by its half-life ($t_{0.5}$; Table 6). In all cases, the dissipation of tiafenacil followed first-order kinetics ($R^2 = 0.8130\text{--}0.9967$). The $t_{0.5}$ dissipation of tiafenacil was in the range of 0.37–3.47 days in 2019 and 0.26–4.19 days in 2020. In 2019, the lowest $t_{0.5}$ value of tiafenacil was observed in Jiangxi (0.37–0.40 day), while the highest was observed in Shandong (3.00–3.47 days). In 2020, the lowest $t_{0.5}$ value was observed in Gansu (0.26–0.36 day), while the highest was in Shandong (2.01–4.19 day). The $t_{0.5}$

TABLE 5 Recovery and standard deviation of tifenacil in five different soil matrices ($n = 5$)

Matrix	Spiked level (mg/kg)	Recovery (%)					Average recovery (%)	Standard deviation	Coefficient of variation (%)
Loessial soil	0.01	87.53	89.91	85.27	89.13	88.20	88.01	1.78	2.02
	0.1	87.43	92.29	88.36	90.87	88.87	89.56	1.98	2.21
	0.5	89.28	97.96	100.01	96.07	96.39	95.94	4.04	4.21
Brown soil	0.01	80.85	82.22	94.25	76.26	97.97	86.31	9.31	10.79
	0.1	85.69	86.23	88.06	87.55	88.51	87.21	1.20	1.38
	0.5	92.97	93.25	94.07	93.17	93.54	93.40	0.43	0.46
Purple soil	0.01	89.51	89.18	89.08	89.58	89.06	89.28	0.25	0.28
	0.1	91.41	93.61	93.74	94.21	93.27	93.25	1.08	1.16
	0.5	88.74	101.87	94.95	100.27	101.74	97.51	5.66	5.80
Red soil	0.01	97.09	100.06	104.85	93.44	104.31	99.95	4.84	4.84
	0.1	99.06	104.69	105.28	99.31	99.97	101.66	3.06	3.01
	0.5	97.35	101.20	103.32	102.42	103.68	101.59	2.56	2.52
Latosol	0.01	80.59	84.00	91.73	87.63	87.79	86.35	4.22	4.89
	0.1	86.97	87.83	87.84	86.15	86.14	86.99	0.85	0.98
	0.5	95.89	94.96	94.27	94.52	94.54	94.84	0.64	0.67

TABLE 6 Dissipation kinetic equation, correlation coefficient (R^2), and half-life ($t_{0.5}$) of tifenacil in citrus orchard soils from five experimental sites

Dosage (g a.i./hm ²)	Year	Location	Dissipation equation	R^2	$t_{0.5}$ (d)
160.50	2019	Gansu	$C_t = 0.1562e^{-1.8356t}$	0.9652	0.38
		Shandong	$C_t = 0.6512e^{-0.2313t}$	0.9894	3.00
		Sichuan	$C_t = 0.0597e^{-1.0972t}$	0.8130	0.63
		Jiangxi	$C_t = 0.0593e^{-1.7282t}$	0.9841	0.40
		Hainan	$C_t = 0.1758e^{-0.4099t}$	0.9208	1.69
	2020	Gansu	$C_t = 0.1950e^{-2.6632t}$	0.9765	0.26
		Shandong	$C_t = 0.9622e^{-0.3444t}$	0.9436	2.01
		Sichuan	$C_t = 0.1272e^{-1.0795t}$	0.9688	0.64
		Jiangxi	$C_t = 0.1811e^{-1.6546t}$	0.9081	0.42
		Hainan	$C_t = 0.2564e^{-0.3167t}$	0.9335	2.19
240.75	2019	Gansu	$C_t = 0.2286e^{-1.6421t}$	0.9953	0.42
		Shandong	$C_t = 0.6085e^{-0.1999t}$	0.9721	3.47
		Sichuan	$C_t = 0.1820e^{-1.2608t}$	0.9947	0.55
		Jiangxi	$C_t = 0.4977e^{-1.8894t}$	0.9526	0.37
		Hainan	$C_t = 0.5771e^{-0.4803t}$	0.9174	1.44
	2020	Gansu	$C_t = 0.3287e^{-1.9390t}$	0.9967	0.36
		Shandong	$C_t = 0.8762e^{-0.1656t}$	0.9689	4.19
		Sichuan	$C_t = 0.1801e^{-1.4105t}$	0.9721	0.49
		Jiangxi	$C_t = 0.5910e^{-1.6107t}$	0.9904	0.43
		Hainan	$C_t = 0.4438e^{-0.3651t}$	0.9532	1.90

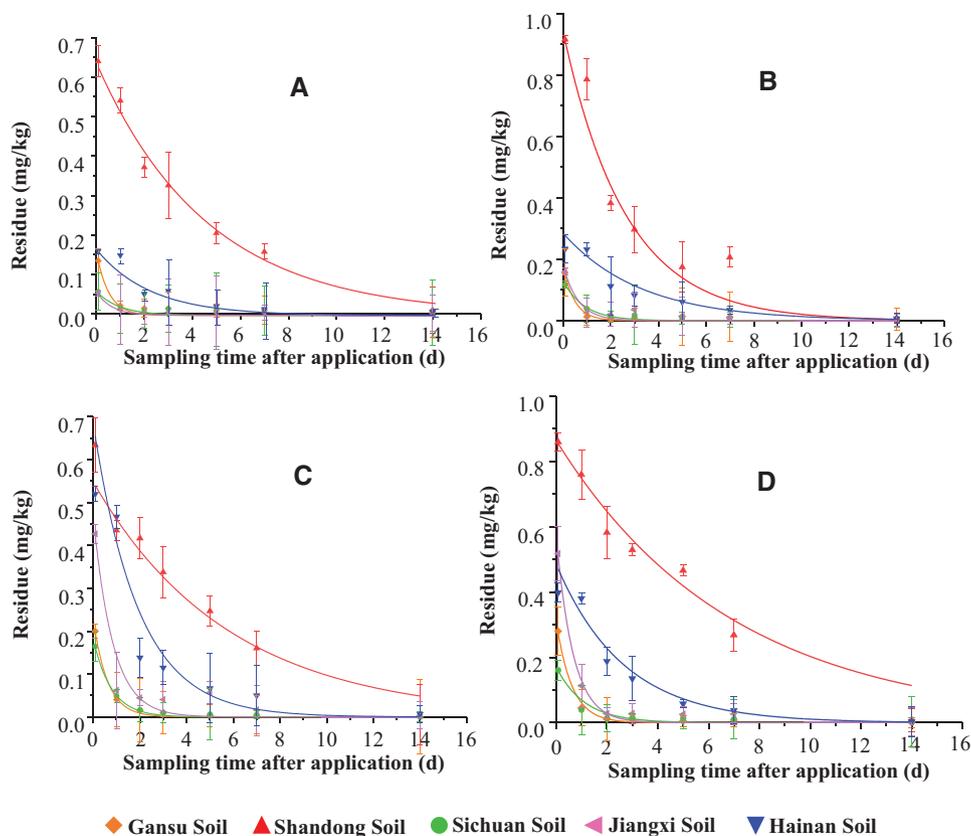


FIGURE 5 Dissipation kinetic curves of tiafenacil in citrus orchard soils from five experimental sites. (A: 2019/160.50 g a.i./hm²; B: 2020/160.50 g a.i./hm²; C: 2019/240.75 g a.i./hm²; D: 2020/240.75 g a.i./hm²)

values of tiafenacil in Gansu, Sichuan, and Jiangxi were generally low, at less than a day. Tiafenacil dissipation was relatively slow in Shandong and Hainan, but the $t_{0.5}$ value was still less than 5 days. Therefore, tiafenacil readily degraded in citrus orchard soils ($t_{0.5} \leq 30$ days) and was environmentally friendly without persistent residues.

The dissipation kinetic curve of tiafenacil was constructed with the sampling time (t) after application as the abscissa and residual concentration (C) as the ordinate. The amount of tiafenacil in soil measured 2 h after the application was taken as the original deposition. At a dosage of 160.50 g a.i./hm², the original deposition of tiafenacil was in the range of 0.0515–0.6397 mg/kg in 2019, and 0.1175–0.9163 mg/kg in 2020. At a dosage of 240.75 g a.i./hm², the original deposition was 0.1645–0.6343 mg/kg in 2019 and 0.1609–0.8591 mg/kg in 2020 (Figure 5). Under the same climatic conditions, a higher dosage of tiafenacil resulted in a higher original deposition in soil. However, differences in the amount of original deposition of tiafenacil were observed across soil types. Under different climates, similar original depositions and dissipation rates of tiafenacil were observed for the same soil type. With passing time, the tiafenacil residue concentrations in soil decreased. The residue

concentrations were less than the LOD 14 days after application. The tiafenacil dissipation rate at different experimental sites was ranked in the following order: Gansu > Sichuan > Jiangxi > Hainan > Shandong. Combined with the results in Table 1, the tiafenacil dissipation rate in soil might be related to soil properties and other factors, but less affected by climatic conditions.

The dissipation rate of pesticides in soil is not only affected by their inherent properties but also soil properties (including organic matter and pH) and climatic conditions [34]. To determine the effects of soil and climatic factors on tiafenacil dissipation in citrus orchard soils, correlations between tiafenacil dissipation half-life and soil organic matter content, soil pH, monthly average temperature, and total rainfall were investigated. The results of linear regression analysis (Table 7) showed that the tiafenacil half-life was negatively correlated with soil pH ($r = -0.5164$ to -0.3938). Therefore, the tiafenacil half-life was shorter and the dissipation rate was faster in alkaline soil. Meanwhile, the tiafenacil half-life was positively correlated with soil organic matter content ($r = 0.8426$ – 0.9210). Therefore, the higher the soil organic matter content, the faster the tiafenacil dissipation rate. However, there was little correlation between tiafenacil dissipation

TABLE 7 Linear regression analysis of the dissipation half-life of tiafenacil in citrus orchard soils with selected soil properties and climatic conditions

Year	Factor	Tiafenacil dosage (160.50 g a.i./hm ²)		Tiafenacil dosage (240.75 g a.i./hm ²)	
		Linear equation	R	Linear equation	r
2019	pH	$y = -0.3631x + 3.5642$	-0.4303	$y = -0.3865x + 3.7451$	-0.3938
	Organic matter	$y = 0.3425x + 0.1006$	0.8887	$y = 0.4018x - 0.0631$	0.8965
	Monthly average temperature	$y = 0.0207x + 0.6775$	0.0872	$y = -0.0006x + 1.2644$	-0.0020
	Total rainfall	$y = 0.0015x + 0.5797$	0.2661	$y = 0.0012x + 0.7469$	0.1798
2020	pH	$y = -0.3547x + 3.4265$	-0.5164	$y = -0.5531x + 5.0959$	-0.4503
	Organic matter	$y = 0.2798x + 0.1722$	0.8426	$y = 0.5469x - 0.3473$	0.9210
	Monthly average temperature	$y = 0.1339x - 2.3765$	0.4819	$y = 0.1068x - 1.3033$	0.2150
	Total rainfall	$y = 0.0024x - 0.1356$	0.4368	$y = 0.0012x + 0.8314$	0.1267

half-life and monthly average temperature or total rainfall at the experimental sites ($r = -0.0020$ to 0.4819).

4 | CONCLUDING REMARKS

This study optimized the QuEChERS sample preparation technique and established an HPLC-MS method to detect tiafenacil residues in citrus orchard soil. A 2-year field dissipation experiment was conducted in five regions across China to determine tiafenacil dissipation in different soil types. The method accuracy and precision were evaluated by recovery test at different spiked levels of tiafenacil (0.01–0.5 mg/kg). The proposed method was fast and simple, taking ~20 min from extraction to detection for each sample. The method sensitivity, accuracy, and precision were satisfactory. Under field conditions, tiafenacil readily dissipated in soil, with the highest dissipation rate observed in Gansu Province (loessial soil) and the lowest in Shandong Province (brown soil). The dissipation half-life of tiafenacil in soil was mainly affected by organic matter and pH, while monthly average temperature and total rainfall had less influence. As tiafenacil is a relatively new herbicide, its residue standards (maximum residue limits) have not been established. This study provides evidence supporting the environmental fate of tiafenacil residues in citrus orchard soil, which is significant for protecting the ecological environment in agricultural systems.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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