Residue characteristics of seven fungicides in cherry tomatoes and vegetable tomatoes

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ABSTRACT

A modified QuEChERS method using a GC-ECD to determine the multiple residues of pyraclostrobin, difenoconazole, dimethomorph and azoxystrobin and to indirectly determine the total residues of maneb, mancozeb and propineb by a GC-FPD (with an S filter) was established and validated. Meanwhile, field trials were conducted in accordance with good agricultural practice (GAP) to study their characteristics of residue degradation under the agricultural climate and cropping system of Guangxi Province. The separation effect of each target peak was good with a linearity range of 0.01–5 mg L⁻¹, a limit of detection (LOD) of 0.003–0.015 mg kg⁻¹ and a limit of quantification (LOQ) of 0.01–0.05 mg kg⁻¹. The average recovery ranges of vegetable tomatoes and cherry tomatoes were 70.5–120.0% and 70.8–119.8%, respectively, with relative standard deviations (RSDs) of less than 7.1%. Field trials of seven fungicides in vegetable and cherry tomatoes showed that the half-lives (t₁/₂) of the dithiocarbamate fungicides (metiram, mancozeb, and propineb, defined as total residues determined as CS₂), pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin were in the ranges of 5.2, 12.7–17.8, 7.6–7.9, 6.6–6.9, and 6.3–6.6 d in vegetable tomatoes, respectively. The cherry tomatoes presented ranges of 4.3–4.5, 10.8–11.8, 6.7–7.0, 5.4–5.5, and 5.9–6.2 d, respectively. Combined with the final residue and market monitoring results, the results show that cherry tomatoes have significantly higher terminal residues, initial deposits, and maximum residues of seven fungicides than vegetable tomatoes, and these seven pesticides can be detected in cherry tomatoes purchased from three markets. Therefore, cherry tomatoes may be regarded as representative varieties of tomatoes in realizing residual extrapolation for the establishment of the maximum residue limit (MRL) value of fungicides in tomatoes and for conducting market monitoring.

KEYWORDS

vegetable tomato, cherry tomato, fungicides, residue characteristics

INTRODUCTION

The tomato plant (Solanum lycopersicum L.) is one of the most important and widely grown vegetable plants; People internationally regard tomatoes as a basic staple food consumed daily in diverse ways, such as raw; cooked; or processed as a canned product, as juice, or as ketchup. Tomatoes have been reported to be associated with several health indicators [1]. According to FAO statistics, China is the world’s leading producer of tomatoes, producing 50 million metric tons [2]. Guangxi Province is one of the most important tomato-producing areas in China in the autumn and winter. Some tomatoes are exported to international markets, such as Russia and Vietnam, every year. Two kinds of tomatoes are grown in China, namely, vegetable and cherry tomatoes [3–4]. However, tomatoes are affected by fungal diseases, insects, nematodes and weeds that can significantly diminish yields or even destroy an entire crop [5–7]. To achieve quality cherry and vegetable tomatoes with high yields, the use of pesticides is considered a necessary, economical and conventional agricultural practice [8–10].
At present, the main varieties of fungicides that have been officially registered in tomatoes in China are as follows: pyraclostrobin, difenoconazole, dimethomorph, azoxystrobin, metiram, mancozeb, etc (https://www.chinapesticide.org.cn/hysj/index.jhtml). Although taking advantage of pesticides can control plant diseases and improve yields, pesticide residues in foodstuffs [11, 12] can pose a risk to human health [13, 14]. Therefore, to better protect the health of consumers, establishing MRLs is necessary. Metiram, mancozeb, etc (https://www.chinapesticide.org.cn/) have been established to have MRLs of 5, 4, 1, and 3 mg kg\(^{-1}\) in China, respectively [15]. The method of pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin extraction from tomatoes by QuEChERS combined with liquid chromatography-tandem mass spectrometry (LC-MS/MS) determination has been reported [16]. However, to our knowledge, no investigations have examined the residue characteristics of pyraclostrobin, difenoconazole, dimethomorph, azoxystrobin, metiram, mancozeb and propineb in these seven fungicides in different varieties of tomatoes, such as in terms of the effect of tomato size (vegetable and cherry tomatoes) or systemic pesticides on pesticide residues.

The objectives of this work were to evaluate the effects of tomato size and pesticide systemic application on vegetable and cherry tomatoes with a GC-ECD or GC-FPD and to provide basic data support for the safe use of pesticides on vegetable and cherry tomatoes.

**EXPERIMENTAL**

**Standards and solvents**

Pyraclostrobin (99.0%), difenoconazole (98.7%), dimethomorph (98.0%), azoxystrobin (98.5%), metiram (78.0%), mancozeb (76.9%) and propineb (70.9%) standard materials were provided by Dr. Ehrenstorfer (Germany). Mancozeb wettable powder (80%) was provided by Shanghai Huiguang Environmental Technology Co., Ltd. (Shanghai, China). Propineb wettable powder (70%) was provided by Bayer Crop Science (Germany). Pyraclostrobin-metiram water dispersing granules (60%) were provided by BASF Europe (Germany). The difenoconazole microemulsion (10%) was provided by the Langfang pesticide pilot plant of the Plant Protection Institute, Chinese Academy of Agricultural Sciences (Langfang, China). Dimethomorph wettable powder (80%) was provided by Shanxi Kanghe Lifeng Biotechnology Pharmaceutical Co., Ltd. (Shanxi, China). Azoxystrobin suspension (250 g L\(^{-1}\)) was provided by Sichuan Lier Crop Science Co., Ltd. (Sichuan, China). Primary secondary amine (PSA) and graphitized carbon black (GCB) were supplied by Agilent Technologies (Santa Clara, CA, USA). Talc powder was purchased from Guangxi Longguang Talc Development Co. Ltd. (Guilin, China). n-Hexane (HPLC grade), stannous chloride and ascorbic acid (analytical grade) were purchased from CNW Technologies GmbH, Germany. Analytical grade sodium chloride, magnesium sulfate anhydrous, acetonitrile, n-Hexane, hydrochloric acid, and acetic acid were purchased from Tianjin Kemiou Reagent Co. Ltd. (Tianjin, China).

**Field experiments and sampling**

The current study was conducted in compliance with the “Standard of Practice for Field Trials of Pesticide Registration Residue” [17] and “Guideline on Pesticide Residue Trials” [18]. The dissipation and final residue experiments were conducted in Nanning (Guangxi Province) from September to January of the following year, and field trials were conducted twice. The average temperature, humidity, and rainfall during the two field trials were 20.4°C, 78.4%, 115.08 mm month\(^{-1}\) and 19.9°C, 85.4%, 109.76 mm month\(^{-1}\), respectively. The climatic indexes were relatively stable during the two field experiments. The experimental area was designed with one test plot and a control plot without pesticide treatment (three replicates). For the dissipation experiment and final residue experiment, the area of the experimental plot was 30 m\(^2\). A buffer area was employed to separate each plot. The dosage (highest recommended dosage of label) application approach is shown in Table 1. Approximately 1 kg of sample was randomly collected from five points in each plot at intervals of 2 h, 1 day, 3, 5, 7, 10, 14, 21 and 28 days after the dissipation experiment. For the terminal residue experiment, the interval of each application was set to 7 days, and approximately 1 kg samples were collected from each plot 3, 5, 7, and 15 days after application. All samples were cut into pieces and homogenized and then stored at \(-20°C\) in a freezer and analysed within a month.

**Sample preparation**

For pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin, 10 g of homogenized sample was weighed in a 100 mL Teflon centrifuge tube, and 10 mL of 1% acetic acid

| Pesticides                        | Supply times | Dose (g a.i./ha) |
|----------------------------------|--------------|-----------------|
|                                  | Dynamic      | Terminal residues |               |
| Mancozeb wettable powder (80%)   | 1            | 3               | 2,895          |
| Propineb wettable powder (70%)   | 1            | 3               | 2,835          |
| Pyraclostrobin-metiram water dispersing granule (60%) | 1 | 2 | 540 |
| Difenoconazole microemulsion (10%) | 1 | 2 | 150 |
| Dimethomorph wettable powder (80%) | 1 | 3 | 300 |
| Azoxystrobin suspension (250 g L\(^{-1}\)) | 1 | 3 | 375 |
in acetonitrile was added. Each sample was extracted with vibration for 3 min. Then, 5 g of sodium chloride was added and shaken for another 2 min before centrifugation at 4500 r/min for 5 min, and 1.5 mL of supernatants was transferred into a 2 mL Teflon centrifuge tube containing 150 mg of magnesium sulfate anhydrous, 50 mg of PSA and 10 mg of GCB. Then, the mixture was vortexed for 2 min and centrifuged at 6,000 r/min for 5 min. Finally, the supernatant was filtered through a 0.22 μm membrane into autosampler vials for GC-ECD analysis.

For metiram, mancozeb, and propinb (the content of pesticides is converted by the amount of conversion from pesticide to carbon disulfide), 5 g of homogenized sample and 0.025 g of ascorbic acid were weighed in a 40 mL headspace bottle, and 15 mL of SnCl₂/5 mol HCl solution and 5 mL of n-hexane were added successively. Then, the bottle was sealed with a PTFE/silicone rubber spacer cap. Each sample was shaken for 30 s and placed in an 80 °C water bath for 2 h and vortexed once every 20 min during this period. The sample was cooled to room temperature before centrifugation at 1,500 r/min for 3 min, and the supernatant was filtered through a 0.22 μm membrane into autosampler vials for GC-FPD analysis.

Carbon disulfide conversion test

Five millilitres of ultrapure water and 0.025 g of ascorbic acid were weighed in a 40 mL headspace bottle with metiram, mancozeb, and propinb at a 0.5 mg L⁻¹ spiked level, and the above steps of metiram, mancozeb, and propinb extraction methods were repeated. To determine the CS₂ chromatographic retention time, standard solutions of carbon disulfide in n-hexane solvent were utilized.

GC analysis

Pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin were analysed with a GC-ECD (Agilent GC 7890A) equipped with a DB-17 capillary column (30 m × 0.25 mm × 0.25 μm). Nitrogen (purity 99.999%) was used as the carrier gas at a constant flow rate of 1.2 mL min⁻¹. The temperature of the injection port was 275 °C, and 1 μL of each sample was injected under the splitless mode. The temperature of the detector was 235 °C, the column temperature was initially set to 100 °C for 2 min, raised to 150 °C at 3 °C min⁻¹, held at this temperature for 1 min, raised to 265 °C at 45 °C min⁻¹, and then held at this temperature for 10 min. The retention time of CS₂ was 16.2 min.

Matrix effect. Standard solution and matrix matched standard solution with gradient concentration were respectively configured to construct standard curve and matrix matched standard curve. Matrix effect = slope(matrix matched standard curve)/slope(standard curve) × 100%.

LOD/LOQ. Take the blank extract of tomato matrix, dilute the mixed standard working solution, and prepare the required matrix matched standard solution step by step. Determine according to the conditions in GC analysis, and draw the matrix matched standard curve with the peak area (y) of each compound as the ordinate and the mass concentration (x) as the abscissa. Take 3 times signal-to-noise ratio (S/N = 3) as LOD and 10 times signal-to-noise ratio (S/N = 10) as LOQ.

Market monitoring of five fungicide residues in vegetable and cherry tomatoes

Eighteen vegetable tomato and 18 cherry tomato samples were randomly selected from three markets (Nanning dancun market, Nanning shuangmaying market and Nanning wuling market), cut into pieces, homogenized and then stored at −20 °C in a freezer before GC analysis.

Statistical analysis

The plotting of residue concentration and time was used to determine the dissipation kinetics of pesticides in vegetable and cherry tomatoes. The dissipation and half-life (t₁/₂) were calculated by the first-order rate equation. The first-order kinetics were further confirmed graphically from equation C / C₀ = e⁻ᵏᵗ, where C₀ represents the concentration of the pesticide residue at time t, C₀ represents the initial concentration after application, and k is the degradation rate constant per day. The half-life (t₁/₂ = ln(2)/k) is calculated from the k value for each experiment. To determine the significant differences (P < 0.05) of residues in vegetable and cherry tomatoes, statistical tests (Duncan test) were applied by IBMSPSS Statistics 19.0.

RESULTS AND DISCUSSION

Method validation

For pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin, in order to reduce the influence of matrix effect (−35% to 14%), the sample extracts were quantified using the matrix matched standard curve. For the other three DTCs fungicides, there was almost no matrix effect in the detection of carbon disulfide, so the quantification of the samples is completed through the standard curve constructed.
by the carbon disulfid standard solution. Good linearity was achieved in the ranges of 0.01–5 (pyraclostrobin, azoxystrobin), 0.01–2 (difenconazole), and 0.05–5 (dimethomorph, CS₂) mg L⁻¹ with five calibration points. The correlation coefficient (R²) was 0.9996–1. And the LOD and LOQ of them were shown in Table 2. Intra and inter-day precision test was performed on all the analytes in the manuscript at the LOQ, medium and high concentration levels. Set five parallel samples for each concentration and determine them continuously for 3 days. Intra and inter-day accuracy was found to be between −6.3% to 3.5% and −3.9% to 1.4%, while Intra and inter-day precision was below 7.1%. The results showed that the method had good reproducibility and stability, and the determination results are reliable. Under the action of SnCl₂/5 mol HCl solution, the average conversion rates of 0.5 mg kg⁻¹ mancozeb, mancozeb and propiozeb to CS₂ were 97.9%, 98.3% and 70.8% respectively, with the RSD was 1.3%, 2.6% and 2.0% respectively. The analytical method described above was verified by recoveries of seven pesticides at three spiked levels with a range of 0.01–5 mg kg⁻¹. For each spiked level, five replicated samples were analysed. The average recoveries of fortified in cherry tomatoes were in the range of 71.8–119.8% with a relative standard deviation (RSD) of below 7.1%. The average recoveries of fortified vegetable tomatoes were in the range of 70.5–118.0% with an RSD of below 6.3%. The average recovery and RSD data are shown in Table 3. The carbon disulfide conversion rates of metiram, azoxystrobin, and propineb ranged from 70.8 to 98.3%, and the relative standard deviation (RSD) ranged from 1.3 to 2.6%. The data on the average

### Table 2. The calibration curves for quantification, correlation coefficient, linear range, LOD and LOQ of five analysis components

| Analysis components | Matrix | Calibration curves | R² | LOD (mg kg⁻¹) | LOQ (mg kg⁻¹) | Linear range (mg kg⁻¹) |
|---------------------|--------|--------------------|----|---------------|---------------|------------------------|
| Pyraclostrobin      | VT     | y = 4574.4x + 276.07 | 0.9997 | 0.003 | 0.01 | 0.01–5 |
|                     | CT     | y = 5907.6x + 14.903 | 0.9998 | 0.003 | 0.01 |          |
| Difenconazole       | VT     | y = 91627x + 400.65 | 1   | 0.003 | 0.01 | 0.01–2 |
|                     | CT     | y = 82436x + 558.92 | 1   | 0.003 | 0.01 |          |
| Dimethomorph        | VT     | y = 14510x + 1108.5 | 0.9996 | 0.015 | 0.05 | 0.05–5 |
|                     | CT     | y = 15225x + 489.23 | 0.9997 | 0.015 | 0.05 |          |
| Azoxystrobin        | VT     | y = 138441x + 4524.7 | 0.9999 | 0.003 | 0.01 | 0.01–5 |
|                     | CT     | y = 142222x + 3916.8 | 0.9993 | 0.003 | 0.01 |          |
| Carbon disulfide    | VT     | y = 4109x + 32.32  | 1   | 0.015 | 0.05 | 0.05–5 |
|                     | CT     | y = 4109x + 32.32  | 1   | 0.015 | 0.05 |          |

VT: Vegetable tomato, CT: Cherry tomato; Except for CS₂, the calibration curves in the table were constructed with matrix matched standard solution.

### Table 3. The average recoveries and relative standard deviation (RSD) in vegetable tomatoes and cherry tomatoes of seven pesticides with three spike levels (n = 5)

| Pesticides       | Spiked level (mg kg⁻¹) | Vegetable tomato | Cherry tomato |
|------------------|-----------------------|------------------|---------------|
|                  |                       | Average recovery/% | RSD/%          | Average recovery/% | RSD/%          |
| Pyraclostrobin   | 0.01                  | 94.3 ± 4.0        | 4.2            | 78.1 ± 3.1        | 4.0            |
|                  | 0.2                   | 115.8 ± 3.9       | 3.3            | 109.7 ± 4.2       | 3.8            |
|                  | 1                     | 116.4 ± 3.9       | 3.3            | 89.9 ± 3.0        | 3.4            |
| Difenconazole    | 0.01                  | 97.0 ± 3.2        | 3.3            | 72.5 ± 2.6        | 3.6            |
|                  | 0.05                  | 98.2 ± 3.7        | 3.8            | 78.9 ± 2.9        | 3.7            |
|                  | 0.5                   | 101.6 ± 3.3       | 3.2            | 107.0 ± 4.5       | 4.2            |
| Dimethomorph     | 0.05                  | 80.6 ± 3.2        | 4.0            | 92.8 ± 3.0        | 3.2            |
|                  | 0.2                   | 96.8 ± 2.9        | 3.0            | 90.1 ± 4.0        | 4.4            |
|                  | 2                     | 104.1 ± 4.3       | 4.1            | 97.0 ± 3.8        | 3.9            |
| Azoxystrobin     | 0.01                  | 70.8 ± 2.3        | 3.3            | 97.8 ± 3.1        | 3.1            |
|                  | 0.2                   | 116.0 ± 4.9       | 4.2            | 117.1 ± 4.9       | 4.2            |
|                  | 2                     | 111.2 ± 2.5       | 2.2            | 104.3 ± 4.6       | 4.4            |
| Metiram          | 0.05                  | 112.0 ± 2.5       | 2.2            | 93.0 ± 5.9        | 6.3            |
|                  | 0.5                   | 70.5 ± 2.4        | 3.3            | 72.7 ± 3.9        | 5.4            |
|                  | 5                     | 120.0 ± 5.1       | 4.2            | 112.8 ± 6.0       | 5.4            |
| Mancozeb         | 0.05                  | 115.9 ± 3.7       | 3.2            | 112.6 ± 5.1       | 4.6            |
|                  | 0.5                   | 70.5 ± 3.5        | 3.0            | 71.8 ± 3.0        | 4.2            |
|                  | 5                     | 117.7 ± 3.2       | 2.7            | 119.7 ± 5.2       | 4.3            |
| Propineb         | 0.05                  | 94.4 ± 5.0        | 5.3            | 119.8 ± 5.6       | 4.7            |
|                  | 0.5                   | 73.8 ± 4.6        | 6.3            | 85.4 ± 6.1        | 7.1            |
|                  | 5                     | 118.0 ± 6.4       | 5.4            | 118.1 ± 6.2       | 5.3            |
conversion rate of carbon disulfide and relative standard deviation (RSD) are listed in Table 4. The representative chromatograms in the experiment were shown in Figs 1 and 2. Therefore, the developed method conforms to the requirements applied China [18], Japan [19], the European Union [20], CAC and OECD of pesticide residues [21, 22].

Dissipation of seven fungicides

The dissipation curves of seven fungicides in vegetable and cherry tomatoes for two field trials are shown in Fig. 3A-E. The half-life ($t_{1/2}$) and $C_t = C_0e^{-kt}$ of residue dissipation are listed in Table 5a-b. The half-lives ($t_{1/2}$) of metiram, mancozeb, propineb (the half-lives of the three dithiocarbamate fungicides were calculated by the sum of carbon disulfide converted from metiram, mancozeb, and propineb), pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin were in the ranges of 5.2, 12.7–17.8, 7.6–7.9, 6.6–6.9, and 6.3–6.6 d in vegetable tomatoes, respectively. $t_{1/2}$ were in the ranges of 4.3–4.5, 10.8–11.8, 6.7–7.0, 5.4–5.5, and 5.9–6.2 d in cherry tomatoes, respectively. We can draw some conclusions from Table 5a-b; on the one hand, seven fungicides in vegetable tomatoes had longer half-lives than in cherry tomatoes. Dithiocarbamates, pyraclostrobin, and dimethomorph were significantly different in the first year of the field trial, and dimethomorph was significantly different in both years. This result may be related to cherry tomatoes having a larger surface area and higher growth rate and stronger photodegradation efficiency and growth dilution rates for pesticides. On the other hand, dithiocarbamate fungicides (metiram, mancozeb, and propineb) had shorter half-lives than the other four fungicides for both the vegetable and cherry tomatoes. These residue characteristics may be due to dithiocarbamate fungicides having no internal absorption or diversified degradation pathways [23]. We must pay more attention to the use of pyraclostrobin, which

Table 4. The average conversion rate of carbon disulfide and relative standard deviation (RSD) of three pesticides in vegetable tomatoes and cherry tomatoes ($n=5$)

| Pesticides | Spiked level/\(\text{mg kg}^{-1}\) | Average conversion rate RSD/% |
|------------|----------------------------------|-------------------------------|
| Metiram    | 0.5                              | 97.9 ± 1.3 1.3                |
| Mancozeb   | 0.5                              | 98.3 ± 2.5 2.6                |
| Propineb   | 0.5                              | 70.8 ± 1.4 2.0                |

Fig. 1. Representative chromatograms in the experiment of pyraclostrobin, difenoconazole, dimethomorph and azoxystrobin. (a: 0.2 mg kg$^{-1}$ mixed standard, b: 0.2 mg kg$^{-1}$ vegetable tomato matched standard, c: CK of vegetable tomato, d: vegetable tomato sample spiked with 0.2 mg kg$^{-1}$, e: vegetable tomato sample of day1, f: 0.2 mg kg$^{-1}$ cherry tomato matched standard, g: CK of cherry tomato h: cherry tomato sample spiked with 0.2 mg kg$^{-1}$, i: cherry tomato sample of day1. Red arrow: pyraclostrobin, Blue clipper: difenoconazole, Green clipper: dimethomorph, Black arrow: azoxystrobin)
has a half-life of over 10 d, as pyraclostrobin is not suitable for use in the middle and later tomato growth stages.

**Initial deposits and maximal residues of seven fungicides**

The initial deposits of seven fungicides in vegetable and cherry tomatoes are presented in Fig. 4, which shows higher initial deposits on cherry tomatoes and significant differences for all seven fungicides in the two field trials relative to those of vegetable tomatoes. This may because cherry tomatoes have more skin area per unit weight to contact pollutants than vegetable tomatoes under the same pesticide spraying conditions. Moreover, the maximum residues of seven fungicides appeared 2 h after the use of pesticides in cherry tomatoes.

**Terminal residues of seven fungicides at four preharvest intervals (PHIs) in vegetable and cherry tomatoes**

The half-life, initial deposits, and maximum residues impact terminal residue levels at specified preharvest intervals (PHIs). The terminal residues of seven fungicides in vegetable and cherry tomatoes at PHIs of 3, 5, 7, and 15 d are shown in Table 5. Through the analysis of data at the four PHIs, the highest terminal residues were reached by the 3rd-day PHIs in field trials, which were 9.24–14.3 (the residues of three dithiocarbamates fungicides were calculated by the sum of carbon disulfide converted from metiram, mancozeb, and propineb), 0.048–0.063, 0.33–0.41, 0.34–0.43, and 0.88–1.02 mg kg\textsuperscript{-1} for vegetable tomatoes, respectively, and the values for cherry tomatoes were 10.96–14.59, 0.076–0.098, 0.31–0.38, 0.68–0.75, and 0.91–1.16 mg kg\textsuperscript{-1}, respectively. Moreover, the terminal residues of metiram, mancozeb, propineb, pyraclostrobin, dimethomorph, and azoxystrobin for cherry tomatoes were higher than those of vegetable tomatoes. To ensure the safety of agricultural products, the concentration of fungicides detected in harvested agricultural products is often lower than the MRL value. The MRLs of metiram, mancozeb, propineb, pyraclostrobin, difenconazole, dimethomorph, and azoxystrobin have been established at 5, 5, 1, 0.5, 1, and 3 mg kg\textsuperscript{-1} in China (https://www.chinapesticide.org.cn/), respectively, and the terminal residues of metiram, mancozeb, propineb, pyraclostrobin, difenconazole, dimethomorph, and azoxystrobin in vegetable tomatoes by the seventh-day PHI in field trials were 1.28–2.96, 0.034–0.031, 0.14–0.19, 0.17–0.18, and 0.28–0.40 mg kg\textsuperscript{-1}, respectively, while those for cherry tomatoes were 2.99–3.02, 0.049–0.051, 0.14–0.20, 0.28–0.31, and 0.47–0.78 mg kg\textsuperscript{-1}, respectively. All of these values are lower than the MRL value recommended in China. Therefore, to reduce
dietary risk, the harvest interval of pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin should be set at 3 days or more, and that of dithiocarbamates (metiram, mancozeb, and propineb) should be set at 7 days or more.

Higher terminal residues appeared in vegetable tomatoes for metiram, mancozeb, propineb, pyraclostrobin, dimethomorph, and azoxystrobin. Meanwhile, metiram, mancozeb, and propineb had the highest terminal residue levels, and

**Table 5a. Dissipation kinetic parameters of seven fungicides in vegetable tomatoes and cherry tomatoes (first field trial)**

| Fungicides        | Vegetable tomatoes | Cherry tomatoes |
|-------------------|--------------------|----------------|
|                   | Dissipation equation |                  |
| Metiram*          | $C_t = 11.437e^{-0.13234t}$ | $C_t = 15.551e^{-0.06459t}$ |
| Mancozeb         | $R^2 = 0.9733$ | 0.9726 |
| Propineb         | $R^2 = 0.9043$ | 0.9724 |
| Pyraclostrobin   | $C_t = 0.05233e^{-0.03941t} + 17.8$ | $C_t = 0.08423e^{-0.06405t} + 10.8$ |
| Difenoconazole   | $C_t = 0.28234e^{-0.08839t} + 7.9$ | $C_t = 0.37854e^{-0.09842t} + 7.0$ |
| Dimethomorph     | $C_t = 0.43751e^{-0.10407t} + 6.6$ | $C_t = 0.78942e^{-0.12603t} + 5.5$ |
| Azoxystrobin     | $C_t = 0.72104e^{-0.10529t} + 6.6$ | $C_t = 1.1685e^{-0.11804t} + 5.9$ |

*In this study, the half-life of three dithiocarbamates fungicides was calculated by the sum of carbon disulfide converted from metiram, mancozeb, and propineb. The superscript of lowercase letters were the results of significant difference analysis in first field trial by one-way ANOVA. Significant level was $P < 0.05, n = 3$. 

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Fig. 3. Dissipation curves of seven fungicides in vegetable tomatoes and cherry tomatoes in two field trials ($n = 3$). (A: metiram, mancozeb, and propineb, defined as total residues determined as CS2, B: Pyraclostrobin, C: Difenoconazole, D: Dimethomorph, E: Azoxystrobin)
pyraclostrobin had the lowest terminal residue levels in the two kinds of tomatoes, echoing the results of initial deposition and maximum residues.

**Detection and residue of five kinds of fungicide residues in vegetable and cherry tomatoes at market**

The detection results of dithiocarbamates (metiram, mancozeb, and propineb), pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin in 18 vegetable tomato and 18 cherry tomato samples over two consecutive months of market monitoring are displayed in **Fig. 5**, which shows that more pyraclostrobin and difenoconazole residues were detected in the cherry tomato samples than in the vegetable tomato samples (33.4% and 16.6%, respectively). However, dithiocarbamates (metiram, mancozeb, and propineb) were more frequently detected in vegetable tomatoes (33.3%) than in cherry tomatoes. It is possible that tomato grey mould (*Botrytis cinerea* Pers.) and tomato anthracnose (*Colletotrichum lycopersici* Ell. et Ev.) disease are more serious in cherry tomatoes, resulting in the broad use of pyraclostrobin and difenoconazole for control, while early blight is more common in vegetable tomatoes, so dithiocarbamates are used more frequently for this variety.

The market monitoring results show that residues of dithiocarbamates (metiram, mancozeb, and propineb), pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin in vegetable and cherry tomatoes were lower than the terminal residues of seven pesticides at the four preharvest intervals (PHIs) in both

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**Table 5b: Dissipation kinetic parameters of seven fungicides in vegetable tomatoes and cherry tomato (second field trial)**

| Fungicides   | Vegetable tomatoes | Cherry tomatoes |
|--------------|--------------------|-----------------|
| Metiram      | Dissipation equation | $C_t = 3.4269e^{-0.1136t}$ | $C_t = 10.79e^{-0.1534t}$ |
|              | $R^2$              | 0.9083          | 0.9729         |
| Mancozeb     | Half-life (d)      | 5.2d            | 4.5d           |
| Propineb     | Dissipation equation | $C_t = 0.03894e^{-0.05446t}$ | $C_t = 0.07713e^{-0.05867t}$ |
|              | $R^2$              | 0.8743          | 0.8052         |
| Pyraclostrobin | Half-life (d)     | 12.7a           | 11.8a          |
| Difenoconazole | Dissipation equation | $C_t = 0.32131e^{-0.09092t}$ | $C_t = 0.83203e^{-0.10355t}$ |
|              | $R^2$              | 0.8785          | 0.9373         |
|              | Half-life (d)      | 7.6b            | 6.7bc          |
| Dimethomorph | Dissipation equation | $C_t = 0.54275e^{-0.1007t}$ | $C_t = 1.6391e^{-0.1285t}$ |
|              | $R^2$              | 0.9414          | 0.9440         |
|              | Half-life (d)      | 6.9bc           | 5.4d           |
| Azoxystrobin | Dissipation equation | $C_t = 2.1509e^{-0.1096t}$ | $C_t = 2.5118e^{-0.11224t}$ |
|              | $R^2$              | 0.8363          | 0.9628         |
|              | Half-life (d)      | 6.3c            | 6.2c           |

*In this study, the half-life of three dithiocarbamates fungicides was calculated by the sum of carbon disulfide converted from metiram, mancozeb, and propineb. The superscript of lowercase letters were the results of significant difference analysis in second field trial by one-way ANOVA. Significant level was $P < 0.05$, $n = 3$.

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**Fig. 4.** Initial concentrations of seven fungicides in vegetable tomatoes and cherry tomatoes in first field trial (A) and second field trial (B). *The superscript of lowercase letters were the results of significant difference analysis in the same year. Significant level was $P < 0.05$, $n = 3$.
Table 6. Final residues of seven fungicides in vegetable tomatoes and cherry tomatoes (mg kg\(^{-1}\)) \((n = 3)\)

| Fungicides (Spray times) | MRLs (China) | Preharvest intervals (d) | Vegetable tomato | Cherry tomato |
|--------------------------|--------------|-------------------------|------------------|--------------|
|                          |              | First field trial       | Second field trial|              |
|                          |              |                         |                  |              |
| Metiram (2)              | 5            | 3                       | 14.30 ± 1.22     | 9.24 ± 0.72  |
|                          |              |                         |                  |              |
| Mancozeb (3)             | 5            | 5                       | 9.88 ± 0.88      | 5.31 ± 0.43  |
|                          |              |                         |                  |              |
| Propineb (3)             | 5            | 3                       | 2.96 ± 0.30      | 1.28 ± 0.10  |
|                          |              |                         |                  |              |
|                          |              | 15                      | 0.50 ± 0.04      | 0.65 ± 0.05  |
| Pyraclostrobin (2)       | 1            | 3                       | 0.06 ± 0.01      | 0.05 ± 0.01  |
|                          |              |                         |                  |              |
|                          |              | 5                       | 0.05 ± 0.01      | 0.04 ± 0.01  |
|                          |              |                         |                  |              |
|                          |              | 7                       | 0.03 ± 0.01      | 0.03 ± 0.01  |
|                          |              |                         |                  |              |
|                          |              | 15                      | 0.02 ± 0.01      | 0.02 ± 0.01  |
|                          |              |                         |                  |              |
| Difenoconazole (2)       | 0.5          | 3                       | 0.41 ± 0.03      | 0.33 ± 0.04  |
|                          |              |                         |                  |              |
|                          |              | 5                       | 0.29 ± 0.03      | 0.28 ± 0.03  |
|                          |              |                         |                  |              |
|                          |              | 7                       | 0.19 ± 0.02      | 0.14 ± 0.01  |
|                          |              |                         |                  |              |
|                          |              | 15                      | 0.12 ± 0.01      | 0.13 ± 0.01  |
| Dimethomorph (3)         | 1            | 3                       | 0.43 ± 0.02      | 0.34 ± 0.02  |
|                          |              |                         |                  |              |
|                          |              | 5                       | 0.27 ± 0.02      | 0.26 ± 0.02  |
|                          |              |                         |                  |              |
|                          |              | 7                       | 0.17 ± 0.01      | 0.18 ± 0.02  |
|                          |              |                         |                  |              |
|                          |              | 15                      | 0.07 ± 0.05      | 0.09 ± 0.01  |
| Azoxyostrobin (3)        | 3            | 3                       | 0.88 ± 0.06      | 1.02 ± 0.10  |
|                          |              |                         |                  |              |
|                          |              | 5                       | 0.45 ± 0.03      | 0.81 ± 0.06  |
|                          |              |                         |                  |              |
|                          |              | 7                       | 0.28 ± 0.02      | 0.40 ± 0.03  |
|                          |              |                         |                  |              |
|                          |              | 15                      | 0.16 ± 0.01      | 0.23 ± 0.02  |

ND: means the concentration of pesticides lower than the limit of detection.
vegetable and cherry tomatoes as suggested above, indicating that the two kinds of tomatoes sold in markets meet the good agricultural practice (GAP) standards (Table 7).

CONCLUSION

The methods applied for the extraction, purification, and estimation of residues were found to be satisfactory both quantitatively and qualitatively. The average recovery of seven fungicides in vegetable and cherry tomatoes ranged from 70.5 to 120.0% and 70.8 to 119.8% with relative standard deviations (RSDs) of 2.2–6.3% and 3.1–7.1% at the three spiked levels, respectively. From the results regarding residues found in supervised field trials in Guangxi Province, dithiocarbamate fungicides (metiram, mancozeb, and propineb) were found with the highest terminal residues, initial deposits and maximum residues on vegetable and cherry tomatoes after application, and cherry tomatoes had higher terminal residues, initial deposits, and maximum residues of seven fungicides with significant differences compared to those of vegetable tomatoes and may be regarded as a representative variety of tomatoes in establishing MRLs for pesticides. Combined with the results of terminal residues and market monitoring, to reduce dietary risk, the harvest intervals of pyraclostrobin, difenoconazole, dimethomorph, and azoxystrobin should be set at 3 days or more, and that of dithiocarbamates (metiram, mancozeb, and propineb) should be set at over 7 days. In a word, the residue characteristics and digestion of seven fungicides in cherry tomatoes and vegetable tomatoes were studied in this paper. It is found that cherry tomato has higher initial residue than large tomato, which suggests that cherry tomatoe may have a higher dietary risk. In the MRL reformulation, cherry tomatoes are more suitable to be selected than vegetable tomatoes to maintain the safety of agricultural products and improve international competitiveness. At the same time, it provides the basis for establishing safety intervals of pesticides commonly used on two kinds of tomato. This study showed that in the same crop with different sizes of individuals, the varieties of small individuals may have more specific surface area and more drug delivery area, which would lead to higher concentration residues, slower digestion rate and higher dietary risk in the case of the same drug application method. Therefore, In the screening of representative crops in residue test, we should pay more attention to the difference of residue risk caused by small individual varieties, so as to avoid the problem of underestimating the safety risk in the calculation of dietary risk assessment. Finally, it should be pointed out that the present trials were conducted in Guangxi, and there was no assessment of dietary risk in vegetable and cherry tomatoes; therefore, more field experiments of pesticides in other provinces or countries and dietary risk assessments are needed.

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