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Determination of the Dissipation Dynamics and Terminal Residue of Bupirimate and Its Metabolites in Cucumber by QuEChERS-Based UPLC-MS/MS

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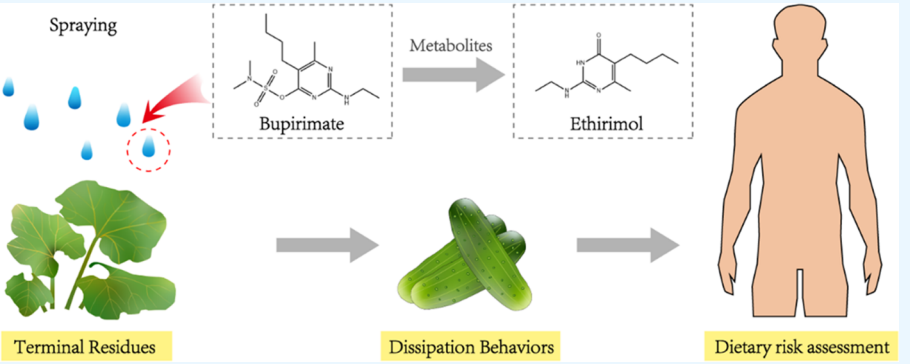

ABSTRACT: Bupirimate is widely used as a highly active systemic fungicide. However, the frequent and heavy use of bupirimate has led to pesticide residues in crops that threaten human health and food safety. At present, there is limited research on the detection of ethirimol, which is the metabolite of bupirimate. This study established an ultrahigh-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) method to simultaneously detect bupirimate and ethirimol residues based on QuEChERS pretreatment. The average recoveries of bupirimate and ethirimol in cucumber were between 95.2 and 98.7%, respectively, with relative standard deviations (RSDs) of 0.92−5.54% at fortified levels of 0.01, 0.1, and 5 mg L^{-1}. The established method was used to determine the residues in field trials in 12 regions of China, and the final residues of bupirimate were all less than the maximum residue limit (MRL). Since the risk quotient (RQ) of bupirimate and ethirimol in cucumber was less than 1.3%, the dietary risk assessment indicated that bupirimate and ethirimol had a low long-term dietary risk to the general population in China. This study provides effective guidance on the proper use of bupirimate in cucumber fields and a reference for establishing the MRL of bupirimate in China.

1. INTRODUCTION

Chemical pesticides have been widely used in agricultural production as well as in the public health field to protect agricultural crops from mitigating diseases, insects, and grasses and to ensure adequate food production to meet the increasing population demand worldwide.[1,2] However, with the unreasonable use of pesticides, the problem of pesticide residues in food has attracted more and more attention.[3] Cucumber is a cash crop that is grown worldwide, and diseases caused by *Sphaerotheca fuliginea*, *Pseudoperonospora cubensis*, and *Corynespora cassiicola* often occur in the cultivation process.[4−8] At present, the prevention and control methods mainly rely on chemical pesticides to control diseases. However, due to the unreasonable use of pesticides, the short maturity period of cucumber fruit, and the insufficient safety interval, pesticide residues often exceed the standard and endanger human health.

Currently, the Joint Meeting on Pesticide Residues (JMPR) does not have a residue definition for bupirimate. According to GB 2763-2021 (National for safety standard-Maximum residue limits for pesticides in food) and "Pesticide Registration Residue Test List of Residues to be Tested and Dietary Risk Assessment Residues for Plant-derived Foods", the residue monitoring of bupirimate is defined as bupirimate, and the dietary risk assessment of bupirimate residues is defined as bupirimate and ethirimol. Bupirimate is a systemic fungicide, and its mechanism of action is to inhibit adenosine deaminase

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(ADA). Because bupirimate can be quickly absorbed by plant roots, stems, and leaves after application, it has the ability to resist pesticide losses caused by environmental factors, and, as a result, it has a long duration and is widely used in the cultivation of fruit trees, vegetables, flowers, and other crops.[9] Ethirimol is one of the metabolites of bupirimate and has the same action mechanism as bupirimate.

At present, the detection methods of bupirimate mainly include gas chromatography (GC), gas chromatography-tandem mass spectrometry (GC-MS/MS), liquid chromatography-tandem mass spectrometry (LC-MS/MS), liquid chromatography-triple quadrupole/mass spectrometry (LC-TQ/MS), and liquid chromatography/electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS),[3,10−13] Compared with traditional methods, the use of ultrahigh-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) has the advantages of being rapid, sensitive, and accurate compared to traditional methods.[14] However, most studies have been limited to the single detection of bupirimate, and there are few studies on ethirimol residues in agricultural crops. In addition, studies on terminal residues, dissipation behavior, and dietary risk assessment in field trials of bupirimate and ethirimol registered that crop cucumbers are still lacking, and it is important to assess the longevity of both compounds and their safety to consumers. The risk assessment of dietary residues of bupirimate and ethirimol in registered crops can provide a scientific basis for the proper use of pesticides, rational regulation, consumer guidance, and the publication and revision of MRL.

In summary, the objectives of this study were (1) to develop and validate a simple and efficient method for the detection of bupirimate and ethirimol in cucumbers; (2) to investigate the terminal residues and dissipation behavior of bupirimate and ethirimol in 12 cucumber production areas in China; (3) to assess the long-term dietary risk to the general population in China; and (4) to provide a theoretical basis for the scientific use of 25% bupirimate microemulsions (MEs) in cucumber production and a reference for establishing the MRL of bupirimate in China.

2. RESULTS AND DISCUSSION

2.1. Optimization of Sample Pretreatment. Cucumbers are rich in proteins, sugars, fats, vitamins, and various trace elements, among others. These different impurities cause a more complicated analysis of the sample matrix. The traditional QuEChERS preprocessing method uses PSA as a purification agent, which is effective in adsorbing sugars, fatty acids, and metal ions from the samples to be tested but less effective in purifying the pigments in cucumbers.[15] In the present study, different combinations of purification materials were used to treat cucumbers for optimal purification results. GCB was able to effectively adsorb the pigment, and the formulation using a combination of PSA and GCB as a purification agent was able to efficiently remove redundant influencing factors in the cucumber matrix.[16−18] In addition, different amounts of purification materials were screened in this study, and the average recovery rate was used to evaluate the purification effect. The average recovery rates of 70−120% were considered excellent, and optimal purification strategies were proposed.

As shown in Figure 1, when different combinations of PSA + GCB were used (10 + 60, 20 + 50, 30 + 40, 40 + 30, 50 + 20, 60 + 10 mg), the average recoveries of bupirimate were 74.9−98.1%, with relative standard deviations (RSDs) of 4.26−6.24%, while the average recoveries of ethirimol were 73.7−115.4% and the RSDs were 3.26−8.26%. These results indicated that a certain amount of GCB was able to adsorb the pigment and improve detection accuracy for the pretreatment of cucumber samples that had a high pigment content. PSA also had a good purification effect on polar impurities and could adsorb vitamins, sugars, and other substances in cucumbers. For this reason, PSA and GCB are recommended as purification agents for vegetable, fruit, or tea crops that have a similar composition to cucumbers. For this study, the optimal combination of purification agents was 50 mg PSA and 20 mg GCB.

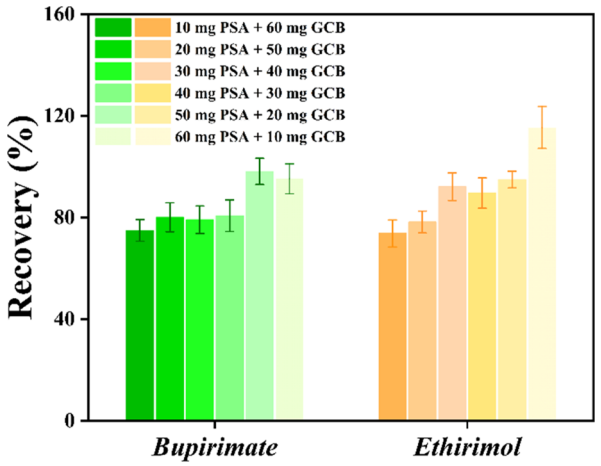

Figure 1. Average recovery of bupirimate and ethirimol under different combinations of purification agents.

2.2. Method Validation. The linearity, matrix effects (ME), reproducibility, and sensitivity of the proposed method were further verified. As shown in Table 1, the mass concentrations of bupirimate and ethirimol showed a good linear relationship with the corresponding peak area within the range of 0.001−0.5 mg L^{-1}, and the correlation coefficient (R^2) was 1.0000. The LOQ of bupirimate and ethirimol on cucumber was 0.01 mg kg^{-1}. The MEs of bupirimate and ethirimol in cucumbers were between 0.8 and 1.2, indicating no significant matrix effect. The best combination of purifying agents (50 mg PSA + 20 mg GCB) was used at fortified levels of 0.01, 1, and 5 mg kg^{-1} for the recovery test of bupirimate and ethirimol in cucumber samples. As shown in Figure 2, the recoveries ranged from 95.2 to 98.7%, with RSDs of 0.92−5.54%.

2.3. Dissipation Behaviors and Terminal Residues of Bupirimate and Ethirimol in Cucumber Samples. The collected samples were determined using the method developed in this study. The dissipation behaviors of bupirimate in cucumbers from Liaoning, Shandong, Jiangsu, and Guizhou provinces were analyzed. Figure 3 shows the dissipation dynamics of bupirimate in the four regions. The digestion curves of bupirimate in the four regions are $y = 2.33e^{-1.21x}$ (Liaoning, $R^2 = 0.9211$, $t_{1/2} = 0.573$ days), $y = 0.858e^{-0.758x}$ (Shandong, $R^2 = 0.8204$, $t_{1/2} = 0.914$ days), $y = 0.341e^{-0.500x}$ (Jiangsu, $R^2 = 0.9986$, $t_{1/2} = 1.39$ days), and $y = 4.01e^{-0.909x}$ (Guizhou, $R^2 = 0.9840$, $t_{1/2} = 0.763$ days). The results showed that the bupirimate used on cucumber in Liaoning had a digestion rate of more than 90% for 1 day; the rate of 3 days digestion in Shandong was more than 90%. In Jiangsu, the 3 days digestion rate was over 50% and the 5 days

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Table 1. Linearity, ME, and LOQ of Bupirimate and Ethirimol

analyte	calibration curve	linear equation	matrix effects	LOQ (mg kg^{-1})
bupirimate	standard	$y = 33040527.5x - 5689.2$	0.97	0.01
	matrix	$y = 32094541.7x - 493.1$		
ethirimol	standard	$y = 21726426.3x + 11211.6$	0.91	0.01
	matrix	$y = 19779527.9x - 16325.4$		

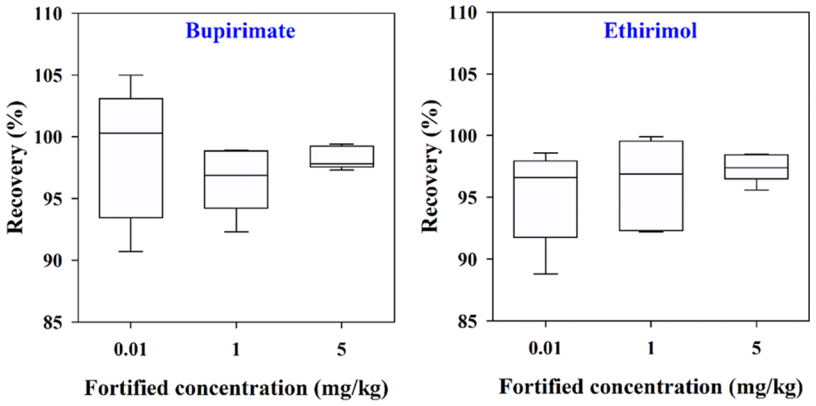

Figure 2. Recoveries of bupirimate and ethirimol in a cucumber matrix at different fortified levels.

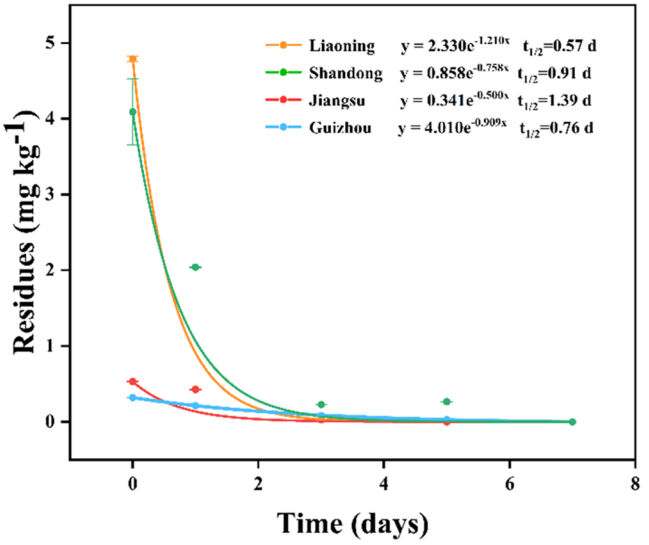

Figure 3. Dissipation behaviors of bupirimate on cucumbers in four regions in China.

digestion rate was over 90%. In Guizhou, the 1 day digestion rate was over 50% and the 3 days digestion rate was over 90%. These results indicated that the bupirimate was rapidly degraded after application. In addition, ethirimol was detected only in the two regions of Liaoning and Guizhou with relatively high residues, indicating that ethirimol was a low proportion of the metabolite of bupirimate.

Table 2 lists the average residual amount of bupirimate in cucumbers from 12 regions. The terminal residue of bupirimate in cucumber differed greatly among provinces. Overall, the terminal residue of bupirimate in northern areas (such as Liaoning and Beijing) was significantly lower than that in southern areas (such as Guangxi and Guangdong). The residue conditions of ethirimol in cucumber were very different from those of bupirimate. As shown in Table 3, ethirimol was detected only in the samples collected from Liaoning, Anhui, and Guizhou.

Table 2. Terminal Residue of Bupirimate on Cucumbers in 12 Regions at an Application Dosage of 300 g a.i. ha^{-1} 3 Times with an Application Interval of 7 Days

		residue (mg kg^{-1})			
test site	harvest interval (days)	repeat 1	repeat 2	repeat 3	average
Liaoning	3	0.0266	0.0255	0.0256	0.0259
	5	<0.01	<0.01	<0.01	<0.01
Shanxi	3	0.106	0.103	0.106	0.105
	5	<0.01	<0.01	<0.01	<0.01
Beijing	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Shandong	3	0.0263	0.0261	0.0262	0.0262
	5	<0.01	<0.01	<0.01	<0.01
Henan	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Anhui	3	0.643	0.625	0.631	0.633
	5	0.227	0.237	0.226	0.230
Jiangsu	3	0.0823	0.0820	0.0823	0.0822
	5	0.0277	0.0278	0.0279	0.0278
Hunan	3	0.479	0.476	0.482	0.479
	5	0.250	0.243	0.245	0.246
Jiangxi	3	0.0261	0.0268	0.0266	0.0265
	5	<0.01	<0.01	<0.01	<0.01
Guangxi	3	0.110	0.108	0.109	0.109
	5	<0.01	<0.01	<0.01	<0.01
Guizhou	3	0.225	0.229	0.227	0.227
	5	0.0256	0.0279	0.0257	0.0264
Guangdong	3	0.109	0.115	0.106	0.110
	5	<0.01	<0.01	<0.01	<0.01

In summary, the pesticides were sprayed at a dosage of 300 g a.i. ha^{-1} three times with an application interval of 7 days. Cucumber samples were collected 3 and 5 days after the last application, and the terminal residue of bupirimate ranged from <0.01 to 0.633 mg kg^{-1}; the terminal residue of ethirimol ranged from <0.01 to 0.202 mg kg^{-1}. The terminal residue

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Table 3. Terminal Residue of Ethirimol on Cucumbers in 12 Regions at an Application Dosage of 300 g a.i. ha^{-1} 3 Times with an Application Interval of 7 Days

test site	harvest interval (days)	residue (mg kg^{-1})			
		repeat 1	repeat 2	repeat 3	average
Liaoning	3	0.125	0.124	0.126	0.125
	5	0.199	0.206	0.201	0.202
Shanxi	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Beijing	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Shandong	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Henan	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Anhui	3	<0.01	<0.01	<0.01	<0.01
	5	0.125	0.128	0.127	0.125
Jiangsu	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Hunan	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Jiangxi	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Guangxi	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01
Guizhou	3	0.154	0.161	0.159	0.158
	5	<0.01	<0.01	<0.01	<0.01
Guangdong	3	<0.01	<0.01	<0.01	<0.01
	5	<0.01	<0.01	<0.01	<0.01

levels of the samples from the 12 regions analyzed in this study were ranked in ascending order, and the results are shown in Tables 4 and 5. The supervised trial median residue (STMR) and the highest residue (HR) of bupirimate were 0.0936 and 0.633 mg kg^{-1}, respectively, and those of ethirimol were 0.01 and 0.158 mg kg^{-1}, respectively. The MRL of bupirimate on cucumbers has not been established in China. The MRL for bupirimate on cucumbers is 2 mg kg^{-1}, according to relevant EU regulations.[19] This study showed that the terminal residues of bupirimate on cucumbers did not exceed the standard and that the recommended dosage of bupirimate was safe for use in cucumber fields.

2.4. Dietary Risk Assessment. Dietary safety was assessed by combining the STMR values obtained in this study with established MRL values of bupirimate and ethirimol on registered crops. The calculation of dietary risk assessment was based on food intake and body weight survey data, combined with pesticide residues in two types of food (light vegetables and fruits) to calculate the NEDI and RQ. According to GB 2763-2021 in China, residue assessment is defined as the assessment of bupirimate and ethirimol. The ADI values of bupirimate and ethirimol are 0.05 and 0.035 mg (kg bw)$^{-1}$, respectively. The registered crops for bupirimate are cucumber and grape, and the registered crops for ethirimol are strawberry, apple, and cucumber. For registered crops without STMRs, the corresponding MRL values should be replaced according to the risk maximization principle to ensure the reliability of the risk assessment. As shown in Table 6, the NEDIs of bupirimate and ethirimol in the general population were 0.04004 and 0.00641 mg, respectively, and the RQs were 1.3 and 0.3%, respectively, which were much lower than 100%; these results indicate that the use of 25% of bupirimate microemulsion under the recommended conditions did not pose an unacceptable risk to the health of the general population. As a metabolite of bupirimate, ethirimol could cause greater food safety problems than bupirimate.[20] Compared with other studies that only consider the dietary risk of bupirimate, the detailed assessment of the two is more comprehensive. Therefore, this study is of great significance for assessing health risks and human food safety.

3. MATERIALS AND METHODS

3.1. Chemicals and Reagents. Reference standards of bupirimate (95.94%) and ethirimol (99.03%) were purchased from BeNa Culture Collection (BeNa, Beijing, China) and Tanmo Quality Inspection Technology Co., Ltd. (Tanmo, Beijing, China). High-performance liquid chromatography (HPLC)-grade methanol and acetonitrile were purchased from Merck (Sigma-Aldrich, Darmstadt, Germany). HPLC-grade formic acid was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Aladdin, Shanghai, China). Analytical grade sodium chloride (NaCl) and anhydrous magnesium sulfate ($MgSO_4$) were purchased from Shanghai Guangnuo Chemical Technology Co., Ltd. (Guangnuo, Shanghai, China) and Tianjin Comious Chemical Reagent Co., Ltd. (Wuhan, Tianjin, China), respectively. Ethylenediamine-*N*-propylsilane (PSA) was purchased from Tianjin Bona Agel Technology Co., Ltd. (Bona Agel, Tianjin, China).

3.2. Sample Collection and Processing. *3.2.1. Field Trials.* The residual dissipation and terminal residue experiments were carried out according to NY/T 788-2018 (guideline for the testing of pesticide in crops). Since the bupirimate microemulsion was only applied to cucumbers, cucumbers were selected as the representatives for residual tests. Terminal residue experiments were conducted in 12 provinces, while residue dissipation tests were conducted in 4 provinces. Detailed information can be found in Table S1 (Supporting Information).

To investigate the terminal and dissipation residue levels of bupirimate, a 25% bupirimate microemulsion was diluted with water (water consumption per hectare is 670 L) and sprayed at a dose level of 300 g active ingredient per hectare (g ha^{-1}), the highest dose registered for cucumber. In the residual test of cucumber powdery mildew, three sprays were applied every 7

Table 4. Terminal Residue of Bupirimate on Cucumbers in 12 Regions and the Corresponding Supervised Trial Median Residue (STMR) and the Highest Residue (HR)

test site	harvest interval (days)	residue (mg kg^{-1})	STMR (mg kg^{-1})	HR (mg kg^{-1})
Liaoning, Shanxi, Beijing, Shandong, Henan, Anhui, Jiangsu, Hunan, Jiangxi, Guangxi, Guizhou, Guizhou	3	<0.01 (2), 0.0259, 0.0262, 0.0265, 0.0822, 0.105, 0.109, 0.110, 0.227, 0.479, 0.633	0.0936	0.633
	5	<0.01 (8), 0.0264, 0.0278, 0.230, 0.246	0.01	0.246

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Table 5. Terminal Residue of Ethirimol on Cucumbers in 12 Regions and the Corresponding Supervised Trial Median Residue (STMR) and the Highest Residue (HR)

test site	harvest interval (days)	residue (mg kg^{-1})	STMR (mg kg^{-1})	HR (mg kg^{-1})
Liaoning, Shanxi, Beijing, Shandong, Henan, Anhui, Jiangsu, Hunan, Jiangxi, Guangxi, Guizhou, Guizhou	3	<0.01 (10), 0.125, 0.158	0.01	0.158
	5	<0.01 (10), 0.127, 0.202	0.01	0.202

Table 6. Calculation Table for the Dietary Risk Assessment of Bupirimate and Ethirimol

pesticide	food types	intake (kg)	residue (mg kg^{-1})	sources of residues	NEDI (mg)	daily intake allowed (mg)	risk probability
bupirimate	light vegetables	0.1837	0.0936	STMR	0.01719	ADI × 63	NEDI/(ADI × 63)
	fruits	0.0457	0.5	residue limit (grape)	0.02285		
	sum	1.0286			0.04004	3.15	1.3%
ethirimol	light vegetables	0.1837	0.01	STMR	0.00184	ADI × 63	NEDI/(ADI × 63)
	fruits	0.0457	0.1	residue limit (apple)	0.00457		
	sum	1.0286			0.00641	2.205	0.3%

days using an electric sprayer, and three replicate plots and one control plot were set up for each treatment (no ethacrynic acid sulfonate, only water). Each plot was 50 m^2 with 1 m wide isolated rows between plots, and 2 kg of cucumber terminal residue test samples was randomly collected 3 and 5 days after the last application. Furthermore, 2 kg of cucumber samples was collected randomly from each plot at 2 h, 1, 3, 5, and 7 days after the last application for dissipation analysis. Three replicate samples were collected each time. Blank controls were randomly selected from untreated test plots prior to application, and finally, all samples were stored at −20 °C until further analysis.

3.2.2. Sample Pretreatment. Cucumber samples were processed using the QuEChERS method as follows:[21,22] all samples were thoroughly ground in a blender; 10.00 g of homogenized cucumber samples was accurately weighed into a 50 mL centrifuge tube, and an exact volume of 20.0 mL of acetonitrile was added and shaken (2500 rpm for 3 min). Subsequently, 3.00 g of NaCl and 2.00 g of $MgSO_4$ were added, followed by shaking (2500 rpm, 3 min) and centrifugation (4000 rpm, 3 min). A total of 1.500 mL of supernatant was transferred to a 2 mL centrifuge tube, prespiked with 50 mg of PSA, 20 mg of GCB, and 130 mg of $MgSO_4$ using the optimal combination of purifying agents; the tube was shaken (2500 rpm for 5 min) and centrifuged (10,000 rpm for 2 min). Finally, the supernatant was diluted 5-fold using acetonitrile, passed through a 0.22 μm membrane filter, and transferred to an autosampler for UPLC-MS/MS analysis.

3.3. Standard Solutions. A certain amount of bupirimate standard and ethirimol standard was accurately weighed, dissolved using acetonitrile, and prepared into a master solution of 1000 mg L^{-1}. The two stock solutions were diluted stepwise in the order of 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 mg L^{-1} using acetonitrile and cucumber blank substrate treatment solution, and all standard solutions were stored at −20 °C.

3.4. UPLC-MS/MS Parameters. A Waters ACQUITY UPLC BEH C18 column (2.1 mm × 50 mm, 1.7 μm) with an electrospray ionization (ESI) source was used for UPLC-MS/MS analysis of bupirimate and ethirimol. The column temperature was 35 °C, the flow rate was 0.30 mL^{-1}, the injection volume was 1 μL, and deionized water containing 0.05% formic acid water and methanol was used as the mobile phase. A gradient elution procedure was performed, and the detailed conditions are listed in Table S2 (Supporting Information). Mass spectrometry was performed using selective reaction monitor (SEM) mode and positive ion mode. The spray voltage was 3500 V, the desolventization temperature was 350 °C, the ion transport tube temperature was 325 °C, the sheath gas pressure was 50 Arb, and the auxiliary gas pressure was 10 Arb. The other detailed parameters are listed in Table 7.

Table 7. Experimental MS Conditions for Bupirimate and Ethirimol

analyte	precursor ion (m/z)	production (m/z)	RF (V)	CE (V)
bupirimate	317.175	272.196	144	23.83
		166.196*		19.15
ethirimol	210.212	140.155	125	26.99
		98.125*		21.98

3.5. Method Validation. According to SANTE/11312/2021 (analytical quality control and method validation procedures for pesticide residue analysis in food and feed),[23] the linearity, ME, reproducibility, sensitivity, and limit of quantitation (LOQ) of the method were verified. The four standard solutions in Section 3.3 were determined based on the analysis conditions in Section 3.4. The standard curve was plotted with the mass concentration of the pesticide to be tested in the standard solution as the abscissa and the corresponding peak area as the ordinate. The ME was evaluated using the slope ratio of the solvent standard curve to the blank matrix standard curve.[24] A ratio of the slope of the matrix standard curve to the slope of the solvent standard curve (k_1/k_2) between 0.8 and 1.2 indicates that there is no evident matrix inhibition effect. When the ratio is less than 0.8, there is a matrix inhibition effect. When the ratio is greater than 1.2, there is a matrix enhancement effect.[25] The recoveries and relative standard deviations (RSDs, %) of the two pesticides were determined by adding 0.01 mg kg^{-1} to a blank matrix using different combinations of purifiers to screen for the best combination of purifiers. In addition, the reproducibility and sensitivity of the method were evaluated using the best combination of purifying agents. Three levels (0.01, 1, 5 mg kg^{-1}) of bupirimate and ethirimol standard solution were added to the blank matrix, with five replicates

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per level. The LOQ is defined as the minimum added concentration.

3.6. Dietary Risk Assessment. The national estimated daily intake (NEDI, mg kg^{-1} day^{-1}) for this pesticide was calculated based on the dietary structure data from "The nutrition and health status of the Chinese people" published by the National Health Commission of the People's Republic of China, combined with the standard residue test median recommended by the residue chemical assessment and the established MRL. The formulas for the calculation are as follows[26,27]

$$\text{NEDI} = \sum [\text{STMRi}(\text{STMR} - \text{Pi}) \times \text{Fi}] \quad (1)$$

$$\text{RQ}\,(\%) = \text{NEDI}/\text{ADI} \times 100\% \quad (2)$$

where STMR (mg kg^{-1}) represents the median concentration of pesticide residues in cucumber in China; STMR-Pi refers to the median concentration of pesticide residues in Chinese cucumbers corrected for processing factors; and Fi (kg^{-1} day^{-1}) refers to the average daily food intake of the general population in China. The ADI (mg kg^{-1} day^{-1}) is the acceptable daily residue level for pesticides specified in GB 2763-2021 (National Food Safety Standard-Maximum residue limits for pesticides in food), where the average weight of a Chinese adult is 63 kg. RQ represents the risk quotient, with RQ $\leq$ 100 indicating an acceptable risk and RQ > 100 indicating an unacceptable risk.[28−30]

3.7. Statistical Analysis. The calculation and analysis of data in the paper were conducted by SPSS Statistics (version 16.0). The means and the standard error (SE) were calculated by Tukey's multiple range test ($p < 0.05$). Origin2022 was used to make the chart analysis.

4. CONCLUSIONS

In this study, the QuEChERS method in combination with the UPLC-MS/MS technique was used to establish a method for the simultaneous detection of bupirimate and ethirimol residues in cucumber. The purification method was optimized using different combinations of purification materials, and the terminal residues and dissipation dynamics of ethirimol sulfonate and ethirimol in agricultural products were determined using the optimal purification method. Through field residue trials in 12 main cucumber-producing areas, the residues of bupirimate and ethirimol in cucumber samples collected 3 and 5 days after the last application were less than 0.633 mg kg^{-1}, and the RQs of bupirimate and ethirimol in cucumber were less than 1.3%. These results indicate a low long-term dietary risk to the general population in China. Overall, these data can provide effective guidance on the proper use of pesticides in cucumber fields, serve as a reference for the development of MRL in China, and contribute to food safety risk management and consumer health.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02644.

Displayed field test sites, crop varieties, and test types (Table S1); and the gradient elution program of UPLC-MS/MS (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

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