

戊唑醇和吡唑醚菌酯在苹果中的残留 行为及膳食暴露风险评估

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摘要:【目的】建立同时检测不同地区苹果中戊唑醇和吡唑醚菌酯的残留分析方法,通过苹果树1年12地的田间试验,监测了2种农药在苹果主要产区的消解态势,并评估不同人群对其膳食暴露风险。【方法】QuEChERS-HPLC-MS/MS法的建立,用于检测苹果中的戊唑醇和吡唑醚菌酯的残留,并且分析2种农药在苹果中的最终残留和消解动态,计算6类典型人群国家估算每日摄入量(National Estimated Daily Intake, NEDI)和风险指数(Risk Index, RI)。【结果】根据戊唑醇和吡唑醚菌酯在苹果中的消解动态,可知2种农药在苹果中的半衰期分别为9.4~21.7 d和10.3~23.8 d。戊唑醇和吡唑醚菌酯在苹果鲜果中膳食暴露RI值均小于100%,膳食暴露风险处于可接受水平,针对6类典型人群进行膳食暴露风险评估,膳食暴露量随年龄的增加逐渐降低。【结论】采用QuEChERS-HPLC-MS/MS法可同时快速检测戊唑醇和吡唑醚菌酯,2种农药在不同年龄段和不同性别人群对于苹果鲜果的膳食暴露风险处于可接受水平,对于农药安全使用和膳食摄入评估具有重要意义。

关键词:苹果; 戊唑醇; 吡唑醚菌酯; 消解; 残留; 膳食风险评估

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Residues behavior and dietary exposure risk assessment of tebuconazole and pyraclostrobin in apple

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Abstract:【Objective】The residue and degradation dynamics of tebuconazole and pyraclostrobin in apple were studied at twelve sites in one year. And the dietary exposure risk assessment concerning two compounds were estimated. 【Methods】QuEChERS-HPLC-MS/MS method was established to detect tebuconazole and pyraclostrobin in apple fruits. The purification of sample was adjusted to the proportion of purifying agent. Samples were extracted by acetonitrile (Compared with methanol, acetonitrile was more efficient and safer as extraction solvent), and purified by a traditional purifying agent (20 mg graphitized carbon black (GCB)+40 mg primary secondary amine (PSA) and 150 mg anhydrous magnesium sulfate). Both compounds were optimized for separating under conditions of chromatography and mass spectrometry. The national estimated daily intake (NEDI) and risk index (RI) of six typical populations were calculated. 【Results】The method established in this study greatly decreased the sample pre-treatment time and the separation efficiency of the two pesticides, the operation was practical, the peak shape was symmetrical, the response value was high and the reproducibility was perfect. In order to achieve efficient purification effect, PSA, PSA + GCB and multi-walled carbon nanotubes (MWCNTs) were investigated in the process of screening out different proportions of purification agents. The amount of purification agent was optimized for obtaining higher recovery. The extraction and purifica-

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tion of apple samples from different regions and varieties could achieve good purification effect. Through addition and recovery test, under three levels of addition (0.005 , 0.5 and $2\text{ mg}\cdot\text{kg}^{-1}$), the average inter-day recovery of tebuconazole in apple matrix was between 87% and 101%, the relative standard deviation (RSDs) ($n=5$) was between 0.6% and 7.9%, the intra-day average recovery was 91%–100%, RSDs ($n=15$) were 1.0%–6.6%; the inter-day average recovery of pyraclostrobin in apple matrix was 87%–103%, RSDs ($n=5$) were 1.3%–7.0%, the average recovery was 93%–101% and RSDs ($n=15$) were less than 6.7%. Compared with other methods, the analytical method established in this study had higher recovery rate and versatility. In practical application group, it could realize rapid detection for a large number of samples from different regions. Moreover, the limit of quantitation about tebuconazole and pyraclostrobin in apple matrix was $0.005\text{ mg}\cdot\text{kg}^{-1}$, which could be used to detect the distribution of two pesticides at low residue level. In this study, the effects of climate conditions and varieties were comprehensively considered. The results of degradation dynamics showed that the half-life period of the two fungicides in apple were faster (In the digestion test plots, the half-life periods of tebuconazole and pyraclostrobin were 9.4–21.7 d and 10.3–23.8 d, respectively), which were easily degradable pesticides ($T_{1/2} < 30$ d). The half-life periods of tebuconazole and pyraclostrobin in apple matrix were influenced by the climate conditions. At the same time, the adhesion of different varieties on apple directly affected the original deposition amount of pesticides, which was one of the important factors affecting pesticide residue behavior. The results of final residue test showed that the residues of tebuconazole and pyrazoxystrobin in apple were 0.010 – $0.191\text{ mg}\cdot\text{kg}^{-1}$ and 0.005 – $0.115\text{ mg}\cdot\text{kg}^{-1}$, respectively, 28 d and 35 d after the last application, which were lower than the maximum residue limits of two pesticides in apple. In addition, according to the final residue data from 12 places in one year, the dietary exposure risk of tebuconazole and pyraclostrobin in fresh apple fruits were calculated. The results showed that the dietary exposure risk index of tebuconazole and pyraclostrobin in fresh apple fruits were less than 100%, and the dietary exposure risk was at an acceptable level. In this study, 12 experimental sites were selected, including main production areas in China. The varieties were local dominant varieties, and the results were more realistic and universal. 【Conclusion】QuEChERS-HPLC-MS/MS method can be used to detect tebuconazole and pyraclostrobin rapidly at the same time. It had prospects applied in the control of raw materials of fresh and processed apples, pesticide residue detection of intermediate processing bodies, spot check of market food quality and national quarantine of imported and exported food. The results showed that the dietary exposure risk of fresh apple was acceptable in six different population, but age and gender had little effect on the overall exposure risk. In different age groups, the dietary exposure risk of 2–4-year-old children was significantly higher than that of additional two groups, which was 3.3–5.6 times and 4.5–5.6 times of the other two groups, respectively. Therefore, in the future food risk assessment, we should take good care of individuals, such as children, women and pregnant women. This study focused on the detection of residues in primary agricultural products, not the processing food. Cleaning, peeling, condensing, sterilization, fermentation and other processes involved in the processing of apple products could be used as the influencing factors of food residues. Therefore, if the processing factors were considered before the assessment of pesticide dietary exposure, more accurate risk assessment would be obtained. The results of this study had reference significance for guiding 40% pyraclostrobin · tebuconazole SC to determine the reasonable safety interval, and was important for the safety of fungicide application and dietary intake evaluation.

Key words: Apple; Tebuconazole; Pyraclostrobin; Dissipation; Residue; Dietary exposure risk assessment

苹果(*Malus domestica* Borkh.)是世界上栽培最为广泛的果树之一,许多国家都将其列为主要消费果品。中国是全球苹果的主产区,苹果产量占到世界总产量的35%^[1-2],因此安全生产对于保证苹果的正常供应有着重要意义。苹果的种植生长过程会遭受很多病害威胁,如苹果斑点落叶病(apple *Alternaria* blotch)在苹果生长季发生频繁,严重影响了苹果的产量和品质^[3-4]。三唑类杀菌剂戊唑醇(Tebuconazole)和甲氧基丙烯酸酯类杀菌剂吡唑醚菌酯(Pyraclostrobin)是防治苹果斑点落叶病的畅销品种,具有不同的作用机制^[5-6]。2种农药通过二元复配结合,可以有效防治多种苹果病害,是农业生产中常用的杀菌剂之一,受到种植者的广泛认可^[7]。但这2种农药长期使用引起的环境和残留问题也值得关注。有研究表明,戊唑醇和吡唑醚菌酯进入水体后均有潜在污染风险,对水生生物、蜂类和蚕类具有不同程度的毒性作用^[8-14],且吡唑醚菌酯在果蔬表面的残留较难除去,易造成食品安全问题^[15]。中国作为苹果的主要消费国,鉴于2种农药产生的影响,明确戊唑醇及吡唑醚菌酯在苹果中残留情况,研究其残留行为,评估膳食暴露风险,对于保障人们的膳食安全有着重要意义。

食品安全国家标准食品中农药最大残留限量(GB 2763—2019)^[16]规定戊唑醇在苹果中的最大残留限量(Maximum Residue Limit, MRL)为2 mg·kg⁻¹,吡唑醚菌酯在苹果中的MRL为0.5 mg·kg⁻¹。关于戊唑醇和吡唑醚菌酯的残留检测方法主要有液相色谱法^[17-21]、液质联用法^[22-26]、气相色谱法^[27-28]和气质联用法^[29-32],其中,同时检测戊唑醇和吡唑醚菌酯的残留对象多集中于玉米、杨梅、香蕉和柑橘中,在对于苹果中2种药剂残留的检测主要涉及单剂或与其他杀菌剂复配。兰丰等^[21]、戚燕等^[25]研究了吡唑醚菌酯在苹果中的残留及消解动态,得到了吡唑醚菌酯在苹果中的半衰期为4.3~23.9 d。丁蕊艳^[30]、罗雪婷等^[31]研究得到了戊唑醇在苹果上的半衰期为4.6~20.7 d。目前,对这2种杀菌剂复配在苹果中的残留检测和风险评估鲜有报道。笔者在前人基础上,采用QuEChERS-HPLC-MS/MS法快速检测戊唑醇和吡唑醚菌酯,对1年12地的苹果样品中2种农药的最终残留量和残留消解趋势进行了深入分析,评价其食用安全性,并以此为戊唑醇和吡唑醚菌酯在苹果生产中的科学使用提供数据支撑。

1 材料和方法

1.1 仪器与试剂

液相色谱-三重四极杆串联质谱仪 Agilent 1290-6460(Agilent)^[33];电子分析天平 ME204(Mettler);高速冷冻离心机 H1850R(湖南湘仪);涡旋振荡器(Scientific Industries);美的料理机 PB10 power206(Midea)。

吡唑醚菌酯(纯度98.6%)和戊唑醇(纯度98.5%)标准品(Dr.Ehrenstorfer);甲酸和乙腈(HPLC grade, ThermoFisher Scientific);石墨化炭黑(GCB)和N-丙基乙二胺(PSA)(Phenomenex);多壁碳纳米管(MWCNTs)(5~10 nm, Macklin);氯化钠和无水硫酸镁(AR grade, Tianjin, China);40%唑醚·戊唑醇悬浮剂(SC, 山东一览科技有限公司)。

1.2 田间试验

试验参照农作物中农药残留试验准则^[34]。供试药剂为40%唑醚·戊唑醇SC,供试苹果均为当地主栽品种,长势良好。试验地信息见表1。

1.2.1 最终残留试验 田间试验设处理和对照小区,试验前后未施用过相同农药。试验药剂以田间推荐最高剂量(有效成分质量分数100 mg·kg⁻¹),稀释后(4000倍液)均匀喷雾,于苹果树苹果斑点落叶病发病初期开始施药,间隔期为7 d(施药次数3次)。样品采集时间为末次施药后28、35 d,首次和末次采集对照样品,每个小区样品采集2份。

1.2.2 残留消解试验 试验在辽宁沈阳、山西运城、山东烟台和新疆阿拉尔4地的最终残留量小区内进行。在第3次施药后2 h及3、7、14、28、35 d采样。

1.3 残留分析方法

1.3.1 样品前处理 前处理提取方法参考文献[35]进行,准确称取10 g匀浆后苹果样品于50 mL离心管中,加入10 mL乙腈,然后涡旋振荡3 min,混匀后加入盐包(4 g无水硫酸镁+1 g氯化钠),涡旋振荡3 min,在4000 r·min⁻¹转速下离心5 min。取1.5 mL上清液,加入预装净化剂(40 mg PSA+20 mg GCB)和无水硫酸镁(150 mg)的2 mL离心管中,涡旋振荡1 min,于5000 r·min⁻¹转速下离心5 min。取上清液,过0.22 μm有机滤膜,待测。

1.3.2 HPLC-MS/MS 检测条件 Agilent Eclipse PlusC₁₈色谱柱(50 mm×2.1 mm, 1.8 μm);柱温40 °C;梯度洗脱程序见表2(A相为甲醇,C相为

表1 试验地信息

Table 1 The information of test site

地点 Site	项目 Item	气候类型 Climate type	品种 Variety
北京昌平 Changping, Beijing	最终残留量 Final residue	暖温带半湿润大陆性季风气候 Semi humid continental monsoon climate in warm temperate zone	富士 Fuji
宁夏银川 Yinchuan, Ningxia	最终残留量 Final residue	大陆性半湿润半干旱气候 Continental semi humid and semi-arid climate	新红星 Starkrimson
安徽宿州 Suzhou, Anhui	最终残留量 Final residue	暖温带半湿润大陆性季风气候 Semi humid continental monsoon climate in warm temperate zone	红富士 Red Fuji
陕西咸阳 Xianyang, Shaanxi	最终残留量 Final residue	暖温带大陆性季风气候 Warm temperate continental monsoon climate	富士 Fuji
陕西渭南 Weinan, Shaanxi	最终残留量 Final residue	暖温带大陆性季风气候 Warm temperate continental monsoon climate	富士 Fuji
河南济源 Jiyuan, Henan	最终残留量 Final residue	暖温带大陆性季风气候 Warm temperate continental monsoon climate	富士 Fuji
山东淄博 Zibo, Shandong	最终残留量 Final residue	暖温带大陆性季风气候 Warm temperate continental monsoon climate	红富士 Red Fuji
新疆阿克苏 Akesu, Xinjiang	最终残留量 Final residue	暖温带极端大陆性干旱荒漠气候 Extreme continental arid desert climate in warm temperate zone	红富士 Red Fuji
辽宁沈阳 Shenyang, Liaoning	最终残留量/消解 Final residue/Dissipation	暖温带大陆性季风气候 Warm temperate continental monsoon climate	寒富 Hanfu
新疆阿拉尔 Alar, Xinjiang	最终残留量/消解 Final residue/Dissipation	暖温带极端大陆性干旱荒漠气候 Extreme continental arid desert climate in warm temperate zone	红富士 Red Fuji
山东烟台 Yantai, Shandong	最终残留量/消解 Final residue/Dissipation	暖温带大陆性季风气候 Warm temperate continental monsoon climate	烟富3号 Yanfu 3
山西运城 Yuncheng, Shanxi	最终残留量/消解 Final residue/Dissipation	暖温带半湿润大陆性季风气候 Semi humid continental monsoon climate in warm temperate zone	美国8号 American No.8

表2 梯度洗脱程序

Table 2 Gradient elution procedure

时间 Time/ min	流动相A Mobile phase A/%	流动相C Mobile phase C/%	流速 Flow rate/ (mL·min ⁻¹)
0.00	10.00	90.00	0.400
0.50	10.00	90.00	0.400
1.50	70.00	30.00	0.400
2.50	70.00	30.00	0.400
3.00	80.00	20.00	0.400
5.00	10.00	90.00	0.400

0.2%甲酸水溶液),进样量1 μL。质谱条件选择ESI⁺和MRM模式。其他质谱参数见表3。

1.3.3 标准溶液的配制及标准曲线绘制 分别准确称取0.01 g(精确至0.000 1 g)的戊唑醇和吡唑醚菌酯标准品,用色谱纯乙腈溶解并定容至100 mL,配制成100 mg·L⁻¹的混合标准储备液。分别用色谱纯乙腈和苹果空白基质对照液逐级稀释,配成0.005、0.01、0.05、0.1、0.5、1、2和5 mg·L⁻¹的系列基质匹配混合标准溶液,现用现配,于4 °C下避光保存。以质量浓度为横坐标,化合物的响应值为纵坐标绘制标

表3 戊唑醇和吡唑醚菌酯主要质谱参数

Table 3 The major MS parameters of tebuconazole and pyraclostrobin

化合物 Compound	母离子 Parent ion	子离子 Daughter ion	裂解电压 Fragmentor/ V	碰撞能量 Collision energies/eV	保留时间 Retention time/min	喷嘴电压 Nozzle/V	毛细管电压 Capillary/V	鞘气温度 Sheath/°C	干燥气温度 Gas/°C
戊唑醇 Tebuconazole	308.2	70.0 ^a	80	20	2.8	500	4 500	350	325
		124.7 ^b	80	40					
吡唑醚菌酯 Pyraclostrobin	388.0	194.1 ^a	85	10	3.0	500	4 500	350	325
		163.1 ^b	85	25					

注:a. 定量离子;b. 定性离子。

Note: a. Quantitative ion; b. Qualitative ion.

准曲线并计算基质效应。

1.3.4 添加回收试验 在空白苹果基质中添加混合标准溶液,添加水平(w)为0.005、0.5和2 mg·kg⁻¹,5次重复。样品前处理和检测方法按照1.3.1和1.3.2进行。计算平均回收率和相对标准偏差。

1.4 数据处理

基质效应(M_E)会导致试验的准确度和精密度下降。本研究中 M_E 按公式(1)计算。当 $M_E > 0$ 时为基质增强效应,反之为基质减弱效应^[36]。

$$M_E / \% = \left(\frac{S_m}{S_s} - 1 \right) \times 100 \quad (1)$$

式中: S_m 为基质匹配标准溶液曲线斜率; S_s 为溶剂标准溶液曲线斜率。

戊唑醇和吡唑醚菌酯在苹果样品中的消解采用一级反应动力学方程进行计算:

$$C = C_0 e^{-kt} \quad (2)$$

$$T_{1/2} = \ln 2 / k \quad (3)$$

式中, C_0 为初始时间的戊唑醇/吡唑醚菌酯质量浓度; C 为 t 时刻时戊唑醇/吡唑醚菌酯质量浓度; k 为消解速率常数。

采用残留中值(Supervised Trials Median Residue, STMR)和农药日允许摄入量(Acceptable daily intake, ADI)按公式(4)和(5)计算^[37-38]。当 $RI < 100\%$ 时,表明膳食风险处于可接受范围。

$$NEDI = \frac{\sum [STMR_i \times F_i]}{bw} \quad (4)$$

$$RI/\% = \frac{NEDI}{ADI} \times 100 \quad (5)$$

式中, $NEDI$ 为国家估算每日摄入量; $STMR_i$ 为残留试验中值; F_i 为一般人群对某一食品的消费量; bw 为人群人均体重; RI 为风险指数; ADI 为农药日允许摄入量。

2 结果与分析

2.1 净化剂的筛选和优化

在样品量均为10 g、添加水平为0.5 mg·kg⁻¹的条件下,考察了不同比例PSA、GCB和MWCNTs净化剂组合的净化效果(图1)。结果表明,当单独使用PSA(30、40和50 mg)作为净化剂时,苹果基质中2种农药的回收率为86%~221%,整体偏高,净化效果差。固定40 mg PSA用量,分别添加10、20和30 mg GCB,考察净化效果,随着GCB用量的不断增加,回收率降低。当选择40 mg PSA+20 mg GCB净化剂组合,净化效果较好,戊唑醇和吡唑醚菌酯的回收率为94%~106%。当MWCNTs单独作为净化剂使用时,考察了5、10、20和30 mg净化剂用量对苹果基质中2种农药的净化效果,由于MWCNTs在吸附杂质的同时,也会吸附目标化合物,因此随着用量的不断增加回收率降低,当使用5 mg MWCNTs时,

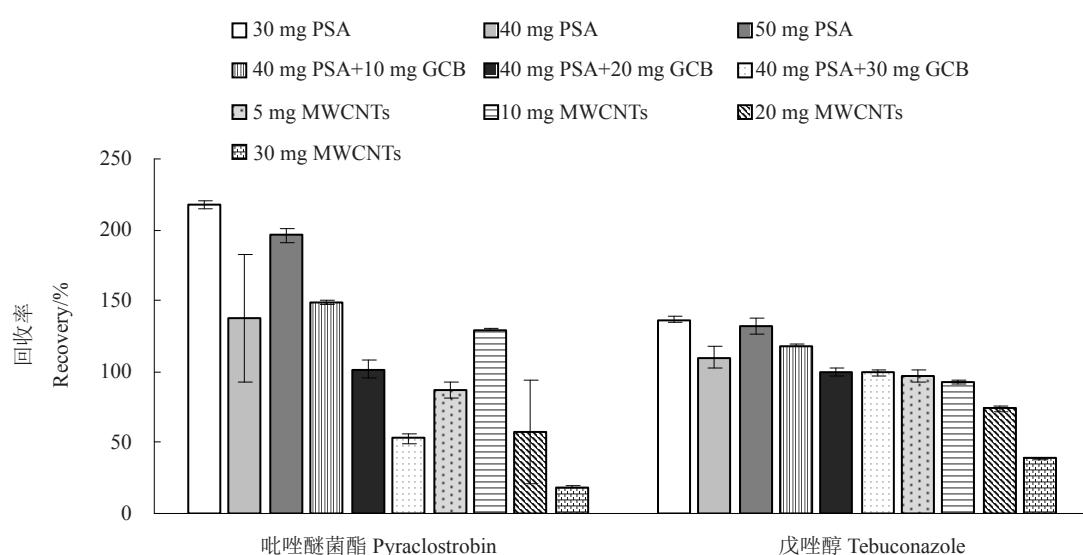


图1 不同净化剂组合下苹果中戊唑醇和吡唑醚菌酯的平均回收率

Fig. 1 Average recoveries of tebuconazole and pyraclostrobin in apples with different purifiers

2种农药的回收率可以达到84%~101%，符合农药残留分析标准。在考虑最优净化效果和较高回收率的情况下，最终选择40 mg PSA+20 mg GCB作为苹果基质中戊唑醇和吡唑醚菌酯的净化剂组合。

2.2 残留检测方法的确证

在0.005~5 mg·L⁻¹线性范围内，2种农药在乙腈和苹果基质中质量浓度与其峰面积间的决定系数R²>0.999 1，线性关系良好，戊唑醇和吡唑醚菌酯在苹果基质中均表现为基质减弱效应，采用外标法

基质匹配标准曲线定量消除基质效应造成的影响，可以确保方法的适用性及通用性^[39]。在3个添加水平下，戊唑醇和吡唑醚菌酯在苹果基质中日内平均回收率为87%~101%和87%~103%，日间平均回收率为91%~100%和93%~101%，相对标准偏差(RSDs)(日内和日间)低于10%，方法验证结果符合残留分析方法要求^[34]。其中，戊唑醇和吡唑醚菌酯在苹果中的定量限(Limit of Quantitation, LOQ)均为0.005 mg·kg⁻¹(表4和表5)。

表4 戊唑醇和吡唑醚菌酯在苹果中的线性范围、定量限及基质效应

Table 4 The linear ranges, quantitative limits and matrix effects of tebuconazole and pyraclostrobin in apple

化合物 Compound	基质 Matrix	线性回归方程 Regression equation	R ²	线性范围 Linear range/(mg·kg ⁻¹)	定量限 LOQ/(mg·kg ⁻¹)	基质效应 Matrix effect, ME/%
戊唑醇 Tebuconazole	乙腈 Acetonitrile 苹果 Apple	y = 86 514x + 883.94 y = 72 069x + 2 544.8	0.999 9 0.999 1	0.005、0.01、0.05、0.1、 0.5、1、2、5	0.005	-
吡唑醚菌酯 Pyraclostrobin	乙腈 Acetonitrile 苹果 Apple	y = 61 058x + 2 062.3 y = 27 716x + 1 387.0	0.999 1 0.999 1			-17 -55

表5 戊唑醇及吡唑醚菌酯在苹果基质中的平均添加回收率和相对标准偏差

Table 5 The recoveries and relative standard deviations of tebuconazole and pyraclostrobin in apple

化合物 Compound	添加水平 Spiked level/ (mg·kg ⁻¹)	日内 Inter-day (n=5)						日间 Intra-day (n=15)	
		1 d		2 d		3 d		回收率	相对标准偏差
		回收率/%	RSDs/%	回收率/%	RSDs/%	回收率/%	RSDs/%	回收率/%	RSDs/%
戊唑醇 Tebuconazole	0.005	90	7.9	90	6.5	87	6.5	91	6.6
	0.500	101	4.8	100	4.8	98	5.8	99	5.1
	2.000	98	4.6	101	0.6	99	0.9	100	1.0
吡唑醚菌酯 Pyraclostrobin	0.005	103	6.6	98	5.3	95	6.6	101	5.4
	0.500	101	5.2	88	1.3	91	2.5	94	6.7
	2.000	94	7.0	87	5.9	96	1.9	93	6.5

2.3 戊唑醇和吡唑醚菌酯在苹果中的消解动态

从消解动态方程(表6)可以看出：在4个试验点中，戊唑醇及吡唑醚菌酯在苹果基质中的消解曲线均符合一级动力学方程，相关系数r>-0.851。

由图2可知，末次施药后2 h，吡唑醚菌酯及戊

唑醇在苹果基质中原始沉积量分别为0.066~0.135和0.229~0.315 mg·kg⁻¹。4地样品于末次施药后7 d，吡唑醚菌酯消解率为1%~15%，戊唑醇消解率为8%~38%，施药后35 d，消解率达到73%~96%(戊唑醇)和66%~93%(吡唑醚菌酯)，残留量逐步减少，消解

表6 戊唑醇及吡唑醚菌酯在苹果中的消解方程及半衰期

Table 6 The dissipation equation and half-life of tebuconazole and pyraclostrobin in apple

化合物 Compound	试验地点 Site	消解动态方程 Dissipation kinetic equation	相关系数 r	半衰期 Half-life/d
戊唑醇 Tebuconazole	辽宁沈阳 Shenyang, Liaoning	c _t =0.240 3e ^{-0.037t}	-0.971	18.7
	新疆阿拉尔 Alar, Xinjiang	c _t =0.345 4e ^{-0.074t}	-0.848	9.4
	山东烟台 Yantai, Shandong	c _t =0.325 0e ^{-0.032t}	-0.934	21.7
	山西运城 Yuncheng, Shanxi	c _t =0.338 7e ^{-0.074t}	-0.851	9.4
吡唑醚菌酯 Pyraclostrobin	辽宁沈阳 Shenyang, Liaoning	c _t =0.127 8e ^{-0.04t}	-0.954	17.3
	新疆阿拉尔 Alar, Xinjiang	c _t =0.117 4e ^{-0.067t}	-0.882	10.3
	山东烟台 Yantai, Shandong	c _t =0.137 8e ^{-0.028t}	-0.930	23.8
	山西运城 Yuncheng, Shanxi	c _t =0.089 7e ^{-0.061t}	-0.894	11.4

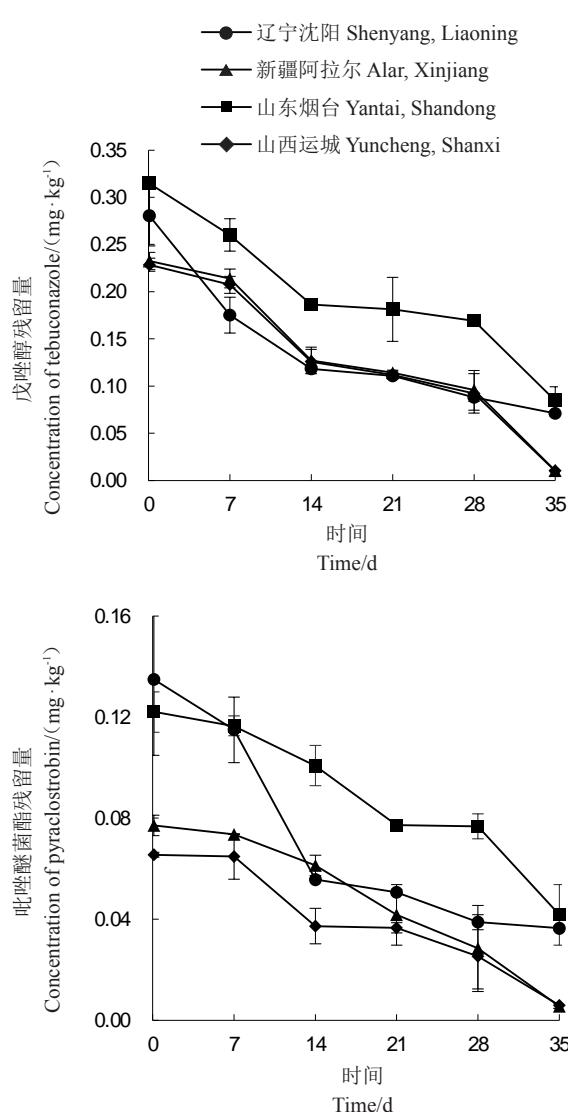


图2 戊唑醇和吡唑醚菌酯在苹果中消解动态曲线

Fig. 2 Dissipation curve of tebuconazole and pyraclostrobin in apple

速率较快。戊唑醇及吡唑醚菌酯在苹果基质中半衰期分别为9.4~21.7和10.3~23.8 d。对比图2中2种农药在4地的消解曲线,吡唑醚菌酯的消解曲线较戊唑醇更趋于平缓,4地中原始沉积量与消解速率存在差异,辽宁沈阳和山东烟台2地的样品中2种农药的消解速率低于其他2地,分析可能与当地气候、苹果品种和种植时期等因素有关。上述结果表明,戊唑醇及吡唑醚菌酯在苹果基质中的消解速率均较快。

2.4 戊唑醇和吡唑醚菌酯在苹果中的最终残留量

40%唑醚·戊唑醇SC在苹果基质1年12地的最终残留量(表7)结果表明,距离末次施药28 d和35 d,苹果中戊唑醇和吡唑醚菌酯的残留量分别为0.010~0.191和0.005~0.115 mg·kg⁻¹,残留中值(STMR)分别为0.083和0.022 mg·kg⁻¹。距离末次施药后28 d和35 d的部分试验地的苹果中戊唑醇的残留量略高于美国制定的戊唑醇在苹果中的MRL值(0.1 mg·kg⁻¹)^[40],对于该种农药的残留在潜在风险。

2.5 膳食风险评估

本研究选择的6类典型人群进行健康风险评估,涵盖了不同年龄段的人群食物摄入量与其体重的差异性,可以准确反映不同人群对2种农药的膳食暴露风险。根据膳食及体重调查数据,与本研究测定的12地苹果中戊唑醇和吡唑醚菌酯最终残留量进行计算,其中STMR值取高值,苹果摄入量采用水果摄入量进行计算^[41],戊唑醇和吡唑醚菌酯的ADI值均为0.03 mg·kg⁻¹。结果(表8)表明,戊唑醇和吡唑醚菌酯在苹果鲜果中膳食暴露风险指数均小于100%。总体来看,膳食暴露量随年龄的增加逐渐降

表7 戊唑醇及吡唑醚菌酯在苹果中的最终残留量($n=2$)Table 7 The terminal residue of tebuconazole and pyraclostrobin in apple ($n=2$)

化合物 Compound	采收间隔期 Interval to harvest/d	最终残留量 Terminal residue/(mg·kg⁻¹)	残留中值 STMR/ (mg·kg⁻¹)		最大残留限量 MRL/(mg·kg⁻¹) 中国 China 国际食品法典 CAC 美国 USA		
			HR/ (mg·kg⁻¹)	最大残留限量 MRL/(mg·kg⁻¹) 中国 China 国际食品法典 CAC 美国 USA			
戊唑醇 Tebuconazole	28	0.019、0.021、0.022、0.023、0.032、0.033、0.041、0.042、0.042、0.043、0.077、0.081、0.085、0.091、0.094、0.107、0.109、0.110、0.166、0.169、0.169、0.172、0.183、0.191	0.083	0.191	2.0	1.0	0.1
	35	0.010、0.010、0.011、0.011、0.011、0.012、0.016、0.017、0.017、0.020、0.020、0.020、0.021、0.021、0.065、0.069、0.073、0.074、0.075、0.088、0.088、0.095、0.102、0.116	0.020	0.116			
吡唑醚菌酯 Pyraclostrobin	28	0.006、0.007、0.007、0.009、0.010、0.011、0.011、0.012、0.013、0.013、0.016、0.016、0.028、0.032、0.035、0.037、0.040、0.041、0.067、0.073、0.074、0.080、0.100、0.115	0.022	0.115	0.5	0.5	8.0
	35	0.005、0.005、0.005、0.005、0.005、0.006、0.007、0.007、0.007、0.008、0.008、0.009、0.009、0.012、0.016、0.033、0.034、0.036、0.037、0.042、0.045、0.047、0.050	0.009	0.050			

表8 中国不同年龄段人群对苹果中戊唑醇和吡唑醚菌酯的膳食暴露风险^[40]
Table 8 The exposure risk of tebuconazole and pyraclostrobin in apple of different agein China

年龄 Age	性别 Gender	体重 BW/kg	膳食摄入量 F/(kg·d ⁻¹)	国家估算每日摄入量 NEDI/(mg·d ⁻¹)		风险指数 RI/%	
				戊唑醇 Tebuconazole	吡唑醚菌酯 Pyraclostrobin	戊唑醇 Tebuconazole	吡唑醚菌酯 Pyraclostrobin
2~4	男 Male	14.1	0.043 7	2.572×10 ⁻⁴	6.818×10 ⁻⁵	0.857 5	0.227 3
	女 Female	13.4	0.044 4	2.750×10 ⁻⁴	7.290×10 ⁻⁵	0.916 7	0.243 0
18~30	男 Male	60.5	0.041 8	5.735×10 ⁻⁵	1.520×10 ⁻⁵	0.191 2	0.050 7
	女 Female	52.6	0.052 9	8.347×10 ⁻⁵	2.213×10 ⁻⁵	0.278 2	0.073 8
60~70	男 Male	61.3	0.033 8	4.577×10 ⁻⁵	1.213×10 ⁻⁵	0.152 6	0.040 4
	女 Female	54.3	0.034 8	5.319×10 ⁻⁵	1.410×10 ⁻⁵	0.177 3	0.047 0

低,儿童(2~4岁)更易受到膳食摄入带来的风险,同年龄段女性较男性更易受影响^[35]。苹果具有丰富的营养、良好的口感和耐储性能等优势,深受人群的喜爱,所以应更加关注特定人群对于通过膳食摄入带来的安全风险。

3 讨 论

本研究建立了QuEChES-HPLC-MS/MS同时检测苹果中戊唑醇和吡唑醚菌酯的残留检测方法,与兰丰等^[21]建立的苹果中吡唑醚菌酯的检测方法和罗雪婷等^[31]建立的苹果中戊唑醇的检测方法相比(戊唑醇和吡唑醚菌酯在苹果中的最小定量限均为0.01 mg·kg⁻¹),前处理条件经过优化,定量限更低($LOQ=0.005 \text{ mg} \cdot \text{kg}^{-1}$),在苹果鲜果以及苹果加工产品生产过程中,有助于产品原料的把控、中间加工体的农药残留检测、市场食品质量的抽查以及国家对于进出口食品的检疫,具有广阔的应用前景^[42]。

多种因素能够影响农药在作物上的残留行为,包括农药自身性质、植物体代谢、果实品种、果实生长过程中稀释因素以及当地气候等。分析本研究中4地进行的消解试验结果,比较4地的原始沉积量,山西运城地区戊唑醇和吡唑醚菌酯在苹果上的原始沉积量均明显小于其他地区,山西运城试验地的苹果品种为美国8号,此品种为美国康奈尔大学培育的优良早熟品种,果实较大且整齐,蜡质层较厚^[43],根据柳璇等^[44]研究,单果体积大可能导致较低的农药原始沉积量,同时该品种具有较厚的蜡质层,也可影响药液在果体上的附着,进而减少农药在果皮上的残留。根据2种农药在苹果中半衰期可知,4地戊唑醇和吡唑醚菌酯的消解速率均为新疆阿拉尔>山西运城>辽宁沈阳>山东烟台。新疆阿拉尔地区苹果中戊唑醇和吡唑醚菌酯的半衰期明显低于其他3

个地区,结合试验点当地暖温带极端大陆性干旱荒漠气候特点,推测戊唑醇和吡唑醚菌酯在苹果中的消解可能与气候有关。通过对比2种农药的消解趋势,4地中2种农药的半衰期差别不大,戊唑醇和吡唑醚菌酯在苹果中的平均半衰期分别为14.8 d和15.7 d,但是山东烟台和辽宁沈阳的戊唑醇和吡唑醚菌酯在苹果中的半衰期均高于其余地方,山东和辽宁同属暖温带大陆性季风气候,所种植的品种为富士,生长期相似,可见气候和品种均能够影响2种农药的消解速率。综合4地消解数据,2种农药在苹果中的消解速率(半衰期分别为9.4~21.7 d和10.3~23.8 d)均较快,为易降解农药($t_{1/2} < 30 \text{ d}$),与已报道的戊唑醇及吡唑醚菌酯在苹果上的半衰期相似(分别为4.6~20.7 d和4.3~23.6 d),此研究结果对于指导40%唑醚·戊唑醇SC合理规定安全间隔期具有参考意义。

分析膳食风险评估数据可知,在各年龄阶段,人们对于戊唑醇的风险指数均高于吡唑醚菌酯。对于不同年龄段人群,幼童对2种农药的风险指数均明显高于其他群体,是其他2类人群的3.3~5.6倍和4.5~5.6倍。同年龄段人群比较,女性略高于男性,因此国家应提高对女性和儿童膳食安全的关注度^[35]。同时,饮食偏好也应被持续关注。在农产品残留水平监测中,本研究通过建立QuEChES-HPLC-MS/MS方法,得到1年12地戊唑醇和吡唑醚菌酯在苹果上的最终残留数据,评估了戊唑醇和吡唑醚菌酯在不同年龄段和不同性别人群对于苹果鲜果的膳食暴露风险,对于杀菌剂安全用药和膳食摄入评估具有重要意义。

4 结 论

本研究建立改进的QuEChES-HPLC-MS/MS方

法,用于同时检测苹果中戊唑醇和吡唑醚菌酯的残留,监测2种农药在低残留情况下的消解趋势。按照推荐剂量施药,戊唑醇和吡唑醚菌酯在6类典型人群中膳食暴露风险处于可接受水平,对于杀菌剂在果树上的安全用药应更加重视。

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