

猕猴桃农药残留膳食摄入风险评估

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摘要:【目的】对猕猴桃中农药残留进行膳食暴露风险评估, 量化常用农药膳食摄入风险水平, 为安全生产、指导消费、安全监管、MRLs制(修)订提供科学依据。【方法】测定某一主产区猕猴桃果实样品中66种农药残留, 分别用%ADI和%ARfD对检出农药进行慢性和急性膳食摄入风险评估, 借鉴英国兽药残留风险排序矩阵进行农药和样品风险排序, 计算最大残留限量估计值(eMRL), 为制定相应农药最大残留限量值(MRL)提供参考。【结果】(1)共检出农药21种, 均为中等毒或低毒农药;(2)检出农药除啶虫脒、灭幼脲无ARfD信息外, 其余19种农药%ADI和%ARfD均明显小于100%;(3)检出农药中溴氰菊酯和毒死蜱为中风险农药($15 \leq S < 20$), 其余均为低风险农药($S < 15$)。98.4%的样品为中、低、极低风险样品;(4)给出了无限量值的噻虫嗪、吡虫啉、甲基硫菌灵等12种农药的最大残留限量估计值eMRL。【结论】检出农药的急、慢性膳食风险均在可接受范围内, 98.4%的样品处于中、低或极低风险区域, 总体来说该主产区猕猴桃质量安全状况良好。建议制定猕猴桃中噻虫嗪等12种农药的MRLs。

关键词: 猕猴桃; 农药残留; 膳食摄入; 风险评估

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Risk assessment of dietary intake of pesticide residues in kiwifruit

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Abstract:【Objective】Risk assessment of dietary exposure to pesticide residues in kiwifruit and quantification of the dietary risk levels of commonly used pesticides provide references for safe production and guidance for consumption of the fruit, food safety supervision, and revision of the Maximum Residue Limits (MRLs) of kiwifruit. 【Methods】Based on detection of the residues of 66 pesticides in 61 kiwifruit samples from a major producing area, chronic dietary intake risk (%ADI) and acute dietary intake risk (%ARfD) of pesticide residues in these samples were assessed. Based on the veterinary drug residue risk ranking matrix constructed by the British Veterinary Drug Residues Committee, the risk of the pesticides and samples was ranked by integrating kiwifruit consumption and pesticide toxicity, frequency of use and residue level, and maximum residue limit estimates (eMRL) were calculated using allowable daily intake (ADI) values, large portion consumed (LP), and body weight (bw). The study will provide a reference for the regulation of the maximum residue limit (MRL) for the corresponding pesticides. 【Results】(1) Among the 62 pesticides, a total of 21 pesticides were detected, and they were low-toxic pesticides except for chlorpyrifos, deltamethrin, cypermethrin and cyhalothrin, which were moderately toxic; (2) Using the pesticide toxicology data, acceptable daily intake (ADI) and acute reference does (ARfD), residual data and kiwifruit consumption data, the risk assessment of the 21 pesticides detected showed that the chronic dietary intake (%ADI) of each pesticide in kiwifruit ranged from 0.000 01% to 0.016 04%. All the 21 pesticides detected but acetamiprid and chlorpyrifos without ARfD informa-

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tion had an acute dietary intake (%ARfD) ranging from 0.01% to 26.20%. The acute dietary intake risk difference between different pesticides was significantly. (3) According to the residual risk score, the 21 pesticides detected were medium- to low-risk pesticides. The risk scores for deltamethrin and chlorpyrifos were 16.5 and 16.1 ie($15 \leq S < 20$), respectively, which were in the medium-risk range. The risk scores of cypermethrin, pyrimidine, buprofezin, cyhalothrin and difenoconazole were between 12.1 and 12.4, and the risk scores of 14 pesticides including procymidone and chlorpyrifos ranged from 8.0 to 9.3 ($S < 15$). All of them were low-risk pesticides. Among the 61 kiwifruit samples, 45.9% of the samples were in a very low risk area with a pesticide residue risk index (RI) below 5; 34.4% of the samples were in a low risk range with a pesticide residue RI between 5 and 10; and 18.0% of the samples were in a medium risk range with a pesticide residue RI of 10 and 15; (4) At present, there were few standard pesticides in kiwifruit. Among the 21 pesticides detected, only carbendazim, acetamiprid, chlorpyrifos, deltamethrin, and cyhalothrin had maximum residue limit (MRL) in kiwifruit or berries and other small fruits in GB 2763—2016, while 76.2% the pesticides had not a limit value. Compared with eMRL, the MRL values of the five pesticides was a more strict parameter related to limitation of quantities. For example, the eMRL of carbendazim was 6.6 times that of MRL; the eMRL of acetamiprid was 3.8 times that of MRL; the eMRL of cyhalothrin was 10.9 times that of MRL; the eMRL of deltamethrin 21.9 times that of MRL; and the eMRL of chlorfenuron was 153 times that of MRL. Among the 21 pesticides detected, carbendazim, acetamiprid, cyhalothrin, deltamethrin and chlorpyrifos had MRLs, and azoxystrobin, chlорfenapyr, malathion, and procymidone had no necessity to formulate MRL. 12 pesticides including thiamethoxam, imidacloprid, thiophanate-methyl, tebuconazole, propiconazole, prochloraz, difenoconazole, buprofezin, trifloxystrobin, chlorpyrifos, cypermethrin and chlorothalonil had no MRLs. 【Conclusion】The pesticides detected were all middle-risk or low-risk pesticides, and the acute and chronic dietary risks of the 21 pesticides were acceptable. At the same time, 98.4% of the 61 samples were at medium, low or very low risk. Therefore, the kiwifruit in the major producing area was relatively safe. It was recommended to develop the MRLs of 12 pesticides including thiamethoxam and imidacloprid for in kiwifruit.

Key words: Kiwifruit; Pesticide residues; Dietary intake; Risk assessment

食品安全严重影响人类生存和生活质量,果品安全在食品安全中占有十分重要的地位^[1-2],而农药残留则是影响果品质量安全的主要因素^[3]。中国是世界猕猴桃起源地,自上世纪七十年代以来,商业化栽培发展迅速,2016年我国猕猴桃产量达到237万t,种植面积和产量均居世界第一位^[4]。生产过程中,猕猴桃主要病害有溃疡病、软腐病、褐斑病、根腐病、灰霉病以及生理性缺素症等,主要虫害有小薪甲、椿象、金龟子、介壳虫、红蜘蛛、根结线虫、蚜虫等。同其他大宗水果一样,猕猴桃在生产过程中化学农药施用是防治病虫害的重要手段和措施,植物生长调节剂^[5-6]、保鲜剂^[7-9]、杀虫剂^[10-13]、杀菌剂^[14-15]等的使用比较普遍,这些化学农药的施用可能会给猕猴桃质量安全带来一定的隐患^[16]。因而开展猕猴桃中农药残留膳食暴露风险评估研究,量化常用农药膳食

摄入风险水平,不仅促进猕猴桃产业安全生产和消费,还可为质量安全监管、最大残留限量(MRLs)制(修)订等提供科学依据,对猕猴桃产业的可持续发展意义重大。

国外水果农药残留风险评估开展较早,目前已有不少报道^[17-20],利用相关评价指标开展农药残留慢性和急性膳食摄入风险评估是其研究重点,而国内水果农药残留风险评估起步较晚,总体报道不多,且多为苹果^[21-23]、桃^[24-25]、葡萄^[26-27]、梨^[28]等大宗水果,利用慢性和急性膳食摄入风险评价指标进行猕猴桃中膳食摄入风险评估还未见报道。

笔者以某主产区为例,对猕猴桃果实中农药残留进行抽样检测,依据相关限量指标进行总体评价,并分别用%ADI和%ARfD对检出农药进行慢性和急性膳食摄入风险评估,同时借鉴英国兽药残留风

险排序矩阵对农药和样品进行风险排序,计算最大残留限量估计值(eMRL),对猕猴桃中必要制定但目前没有最大残留限量的农药提出制定相应的最大残留限量值的建议,以期为相关研究提供有益借鉴。

1 材料和方法

1.1 样品采集

猕猴桃果实样品自2018年9月至11月分别采自某主产区61个典型基地、合作社等,品种涉及‘红阳’‘金桃’‘金艳’‘海沃德’等主栽品种。

1.2 取样验证因子及评估依据

验证因子包括植物生长调节剂、杀虫剂、杀菌剂和除草剂等共66种农药(表1),主要选择对象为我国禁限用和高毒农药以及水果生产中常用农药。评估依据首先参考GB 2763—2016^[29]限量要求,有针对猕猴桃限量要求的直接采用,没有猕猴桃限量要求的参考浆果类水果或者其他水果的限量,对我国GB 2763—2016中没有规定限量标准的优先参照CAC规定的限量标准,CAC中也没规定的参照日本相关限量标准^[16]。

表1 验证因子及测定方法

Table 1 Verification factor and methods for measurement

农药类别 Pesticide type	农药名称 Pesticide name
禁限用和高毒农药 Forbidden and high-toxic pesticides	甲胺磷、甲基对硫磷、对硫磷、久效磷、治螟磷、蝇毒磷、特丁硫磷、灭线磷、甲基异柳磷、甲拌磷、克百威(及其代谢产物:3-羟基克百威)、涕灭威(及其代谢产物:涕灭威砜、涕灭威亚砜)、灭多威、氧乐果、杀扑磷 Methamidophos, Parathion-methyl, Parathion, Monocrotophos, Sulfotep, Coumaphos, Terbufos, Ethoprophos, Isofenphos-methyl, Phorate, Carbofuran(And its metabolite 3 hydroxy carbofur), Aldicarb(And its metabolite aldicarb sulfone and aldicarb sulfoxide), Methomyl, Omethoate, Methidathion
杀虫剂 Insecticide	抗蚜威、吡虫啉、除虫脲、灭幼脲、敌百虫、啶虫脒、虫酰肼、氯虫苯甲酰胺、毒死蜱、乙酰甲胺磷、辛硫磷、亚胺硫磷、杀螟硫磷、马拉硫磷、敌畏、倍硫磷、氯氰菊酯、氰戊菊酯、溴氰菊酯、氯菊酯、氯氟氰菊酯、联苯菊酯、甲氰菊酯、多杀霉素、异丙威、三氯杀螨醇、肟菌脂、噻嗪酮 Pirimicarb, Imidacloprid, Diflubenzuron, Chlorbenzuron, Trichlorfon, Acetamiprid, Tebufenozone, Chlorantraniliprole, Chlorpyrifos, Acephate, Phoxim, Phosmet, Fenitrothion, Malathion, Dichlorvos, Fenthion, Cypermethrin, Fenvalerate, Deltamethrin, Permethrin, Cyhalothrin, Bifenthrin, Fenpropothrin, Spinosad, Isopropcarb, Dicofol, Trifloxystrobin, Bu-profezin
杀菌剂 Fungicide	苯醚甲环唑、异菌脲、甲霜灵、戊唑醇、多菌灵、甲基硫菌灵、咪鲜胺、醚菌酯、代森锰锌、五氯硝基苯、抑霉唑、百菌清、腐霉利、嘧菌酯、乙烯核利、嘧霉胺、丙环唑、肟菌脂 Difenoconazole, Iprodione, Metalaxyl, Tebuconazole, Carbendazim, Thiophanate-methyl, Prochloraz, Kresoxim-methyl, Mancozeb, Quintozene, Imazalil, Chlorothalonil, Procymidone, Azoxystrobin, Vinclozolin, Pyrimethanil, Propiconazole, Trifloxystrobin
杀螨剂 Acaricide	哒螨灵、阿维菌素 Pyridaben, Abamectin
植物生长调节剂 PGR	赤霉素、氯吡脲、2,4-D Gibberellin, Forchlorfenuron, 2,4-D

注:测定依据。GB/T 20769—2008^[30], GB 23200.8—2016^[31], NY/T 761—2008^[32]。
Note: Testing base. GB/T 20769—2008^[30], GB 23200.8—2016^[31], NY/T 761—2008^[32].

1.3 评估过程

1.3.1 急性膳食摄入风险评估过程 急性膳食暴露评估是计算在一天食物消费中摄入的食物和水中的某物质残留量,并对一般人群和特殊亚人群的摄入情况进行风险评估。分别用公式(1)计算农药的估计短期摄入量(NESTI)、公式(2)计算农药的急性膳食摄入风险(%ARfD)、公式(3)计算安全界限(SM)^[33-34]。界定当%ARfD<100%时表示风险可以接受,%ARfD越小风险越小;反之当%ARfD>100%时,表示有不可接受的风险,%ARfD越大风险越大。

$$\text{NESTI} = \frac{U \times \text{HR} \times V + (\text{LP} - U) \times \text{HR}}{\text{bw}}, \quad (1)$$

$$\% \text{ARfD} = \frac{\text{NESTI}}{\text{ARFD}} \times 100; \quad (2)$$

$$\text{SM} = \frac{\text{ARFD} \times \text{bw}}{\text{U} \times \text{VD} + \text{LP} - \text{U}}. \quad (3)$$

式中:NESTI(national estimated short-term intake)为农药的估计短期摄入量,单位kg;U为平均单果质量,单位kg(猕猴桃取值为0.083 kg);HR(highest residue)为农药最高残留量,取99.9百分位点值,单位mg·kg⁻¹;v为变异因子,取值为3;LP(large portion consumed)为消费大份餐,单位kg(猕猴桃^[35]为0.548 7 kg);bw(bodday weight)为体重,单位kg(成人为60 kg);ARFD(acute reference does)为农药急性参考剂量,单位mg·kg⁻¹;SM(safety margin)为农药安全界限,单位mg·kg⁻¹。

1.3.2 慢性膳食摄入风险评估过程 慢性膳食摄入风险评估指对一般人群和特殊亚人群的化学污染物

长期(慢性)膳食暴露情况进行风险评估。用公式(4)计算各农药的慢性膳食摄入风险(%ADI)^[33-34],界定当%ADI≤100%时,表示慢性风险可以接受,%ADI越小,风险越小;%ADI>100%时,表示慢性风险不可以接受,%ADI越大,风险越大。

$$\%ADI = \frac{STMR \times 0.0095}{bw} / ADIx100. \quad (4)$$

式中:STMR(supervised trials median residue)为规范试验残留中值,取平均残留值,单位mg·kg⁻¹;0.0095为居民日均猕猴桃消费量,单位kg;ADI(acceptable daily intake)为农药每日允许摄入量^[29],单位mg·kg⁻¹。

1.4 风险排序

借鉴英国兽药残留委员会兽药残留风险排序矩阵^[36],综合猕猴桃消费及农药毒性、毒效、使用频率、残留水平等因素,计算风险因子农药风险得分S和样品的风险指数RI^[23],对猕猴桃产品中有检出的农药残留情况进行风险排序。分别用公式(5)计算农药风险得分(S)、公式(6)计算农药残留风险指数(RI):

$$S=(A+B) \times (C+D+E+F); \quad (5)$$

$$RI=\sum_{i=1}^n S_i - TS_0. \quad (6)$$

式中:A为农药毒性得分(低毒为2,中毒为3,高毒为4,剧毒为5);B为农药毒效得分(即ADI值>1×10⁻² mg·kg⁻¹为0,ADI值在1×10⁻⁴与1×10⁻³ mg·kg⁻¹之间为1,ADI值在1×10⁻⁶与1×10⁻⁴ mg·kg⁻¹之间为2,ADI值在<1×10⁻⁶ mg·kg⁻¹为3);C为膳食比例得分(<2.5%为0,2.5%~20%为1,20%~50%为2,50%~100%为3,猕猴桃膳食比例0.9%,C得分为0);D为农药使用频率得分(指果实发育期间农药使用次数,猕猴桃用药一般不超过2次,D得分按0计);E为高暴露人群得分(有或无相关数据得分为3,很可能得分为2,无得分为0。此处按有或无相关数据计,E得分为3);F为残留水平得分(未检出得分为1,测定值<1倍MRL得分为2,测定值≥1倍MRL得分为3,测定值≥10倍MRL得分为4);n为检出农药种类个数;TS₀为n种农药均未检出的样品的残留风险得分^[23]。

根据农药残留风险得分(S)将各农药风险大小划分为3类^[23]:第1类为高风险农药,S≥20.0;第2类为中风险农药,15.0≤S<20.0;第3类为低风险农药,S

<15.0;根据样品中农药残留风险指数(RI)将样品分为4类:第1类为高风险样品,RI≥15;第2类为中风险样品,10≤RI<15;第3类为低风险样品,5≤RI<10;第4类为极低风险样品,RI<5。

1.5 农药最大残留限量估计值

为保护消费者,理论最大日摄入量应不大于每日允许摄入量^[23]。因而按公式(7)计算最大残留限量估计值(eMRL):

$$eMRL = \frac{ADI \times bw}{F}. \quad (7)$$

式中:eMRL(maximum residue limit estimate)为农药最大残留限量估计值,单位mg·kg⁻¹;F为猕猴桃日消费量,按照最大风险原则,取大份餐(LP),单位kg;ADI为农药每日允许摄入量,单位mg·kg⁻¹;bw为体重,单位kg(成人按60 kg)。

1.6 数据处理

运用Microsoft excel 2010 和 SPSS21.0 进行数据分析与制图。

2 结果与分析

2.1 农药残留检出情况

猕猴桃果实样品中66种农药共检出21种,结果见表2。其中毒死蜱、溴氰菊酯、氯氰菊酯、氯氟氰菊酯4种农药为中等毒,其余均为低毒农药。检出的21种农药中,GB 2763—2016仅对多菌灵、啶虫脒、氯吡脲、溴氰菊酯、氯氟氰菊酯5种农药制定了最大残留限量值^[29],其余16种农药没有限量值,占76.2%。

2.2 农药残留膳食暴露风险评估结果

利用农药毒理学数据(ADI值、ARfD值)、残留数据和猕猴桃消费数据对检出的21种农药进行膳食暴露风险评估,结果见表3。可以看出,研究范围内猕猴桃中各农药的慢性风险指数(%ADI)在0.000 01%~0.016 04%,均远低于100%。根据膳食暴露风险评估原则,慢性膳食摄入风险(%ADI)越小该农药风险越小,当%ADI≤100%时,表示风险可以接受,说明该主产区猕猴桃农药残留慢性膳食摄入风险是可以接受的,并且都很低。同时根据世界卫生组织(World Health Organization, WHO)数据库^[37],除了啶虫脒、灭幼脲无ARfD信息外,从其余19种农药的ARfD^[38]信息可以看出,研究范围内各农药的急性风险指数(%ARfD)在0.01%~26.20%,

表2 猕猴桃中21种农药残留水平

Table 2 Residue levels of 21 pesticides in kiwifruit

农药 Pesticide	毒性 Toxicity	MRL/ (mg·kg ⁻¹)	残留水平 Residue level/ (mg·kg ⁻¹)	平均 Average/ (mg·kg ⁻¹)
噻虫嗪 Thiamethoxam	低毒 Low	0.2(Water mellon)	ND-0.030 7	0.000 5
多菌灵 Carbendazim	低毒 Low	0.5	ND-0.051 5	0.004 4
吡虫啉 Imidacloprid	低毒 Low	0.5(Japan)	ND-0.1251	0.005 9
啶虫脒 Acetamiprid	低毒 Low	2(Berry)	ND-0.0064	0.0002
甲基硫菌灵 Thiophanate-methyl	低毒 Low	3(Grape)	ND-0.5877	0.021 9
氯吡脲 Forchlorfenuron	低毒 Low	0.05	ND-0.0756	0.009 5
嘧菌酯 Azoxystrobin	低毒 Low	5(CAC)	ND-0.1958	0.004 9
戊唑醇 Tebuconazole	低毒 Low	2(Grape)	ND-0.0894	0.003 7
灭幼脲 Chlorbenzuron	低毒 Low	3(Vegetable)	ND-0.0508	0.000 8
丙环唑 Propiconazole	低毒 Low	0.05(Japan)	ND-0.0135	0.000 2
咪鲜胺 Prochloraz	低毒 Low	2(Grape)	ND-0.0012	0.000 0
苯醚甲环唑 Difenoconazole	低毒 Low	0.5(Grape)	ND-0.2403	0.010 1
噻嗪酮 Buprofezin	低毒 Low	1(Japan)	ND-0.0415	0.001 0
肟菌酯 Trifloxystrobin	低毒 Low	0.1(Banana)	ND-0.0178	0.000 9
毒死蜱 Chlorpyrifos	中等毒 Moderate	2(Japan)	ND-0.2648	0.005 5
溴氰菊酯 Deltamethrin	中等毒 Moderate	0.05	ND-0.1620	0.004 8
氯氰菊酯 Cypermethrin	中毒 Moderate	2(Japan)	ND-0.1410	0.002 8
马拉硫磷 Malathion	低毒 Low	2(Japan)	ND-0.0800	0.001 3
氯氟氰菊酯 Cyhalothrin	中等毒 Moderate	0.2(Berry)	ND-0.4450	0.014 0
百菌清 Chlorothalonil	低毒 Low	0.2(Japan)	ND-0.1140	0.002 2
腐霉利 Procymidone	低毒 Low	3(Japan)	ND-2.3400	0.038 4

但均远低于100%。不同农药之间,急性膳食摄入风险差异明显,如氯氟氰菊酯和腐霉利的%ARfD大于25%,分别为25.43%和26.20%,而噻虫嗪、丙环唑、咪鲜胺、噻嗪酮、肟菌酯、马拉硫磷6种农药的%ARfD均不足1%。根据膳食暴露风险评估原则,即急性膳食摄入风险(%ARfD)越小该农药风险越小,当%ARfD≤100%时,表示风险可以接受^[33],19种农药的%ARfD值远低于100%,表明该主产区猕猴桃农药残留急性膳食摄入风险是可以接受的,并且都

表3 农药慢性风险指数和急性风险指数

Table 3 Risk of chronic intake of pesticides and risk of acute intake

农药 Pesticide	慢性风险评估 Chronic risk assessment		急性风险评估 Acute risk assessment	
	ADI/ (mg·kg ⁻¹)	% ADI	ARfD/ (mg·kg ⁻¹)	% ARfD
噻虫嗪 Thiamethoxam	0.08	0.000 10	0.5(Germany)	0.07
多菌灵 Carbendazim	0.03	0.002 32	0.1	0.61
吡虫啉 Imidacloprid	0.06	0.001 57	0.4(WHO)	0.37
啶虫脒 Acetamiprid	0.07	0.000 04	-	-
甲基硫菌灵 Thiophanate-methyl	0.08	0.004 34	0.2(EPA)	3.46
氯吡脲 Forchlorfenuron	0.07	0.002 15	0.1(WHO)	0.87
嘧菌酯 Azoxystrobin	0.2	0.000 39	0.18(EPA)	1.25
戊唑醇 Tebuconazole	0.03	0.001 93	0.1(Germany)	1.02
灭幼脲 Chlorbenzuron	1.25	0.000 01	-	-
丙环唑 Propiconazole	0.07	0.000 05	0.3	0.05
咪鲜胺 Prochloraz	0.01	0.000 05	0.1(WHO)	0.01
苯醚甲环唑 Difenoconazole	0.01	0.016 04	0.3(WHO)	0.94
噻嗪酮 Buprofezin	0.009	0.001 69	0.67(EPA)	0.07
肟菌酯 Trifloxystrobin	0.04	0.000 37	2.5(EPA)	0.01
毒死蜱 Chlorpyrifos	0.01	0.008 75	0.1(WHO)	3.02
溴氰菊酯 Deltamethrin	0.01	0.007 61	0.05(WHO)	3.69
氯氰菊酯 Cypermethrin	0.02	0.002 21	0.04(WHO)	4.00
马拉硫磷 Malathion	0.3	0.000 07	2(WHO)	0.04
氯氟氰菊酯 Cyhalothrin	0.02	0.011 10	0.02(WHO)	25.43
百菌清 Chlorothalonil	0.02	0.001 77	0.6(WHO)	0.22
腐霉利 Procymidone	0.1	0.006 07	0.1(WHO)	26.20

很低。

2.3 农药残留风险排序

借鉴英国兽药残留委员会兽药残留风险排序矩阵,综合猕猴桃消费及农药毒性、毒效、使用频率、残留水平等因素,根据公式(5)计算各风险因子农药的风险得分,对猕猴桃产品中检出的农药残留情况进行风险排序。从图1中可以看出,溴氰菊酯和毒死蜱的风险得分最高,S分别为16.5和16.1,即15≤S≤20,为中风险农药;氯氟氰菊酯、咪鲜胺、噻嗪酮、氯氟

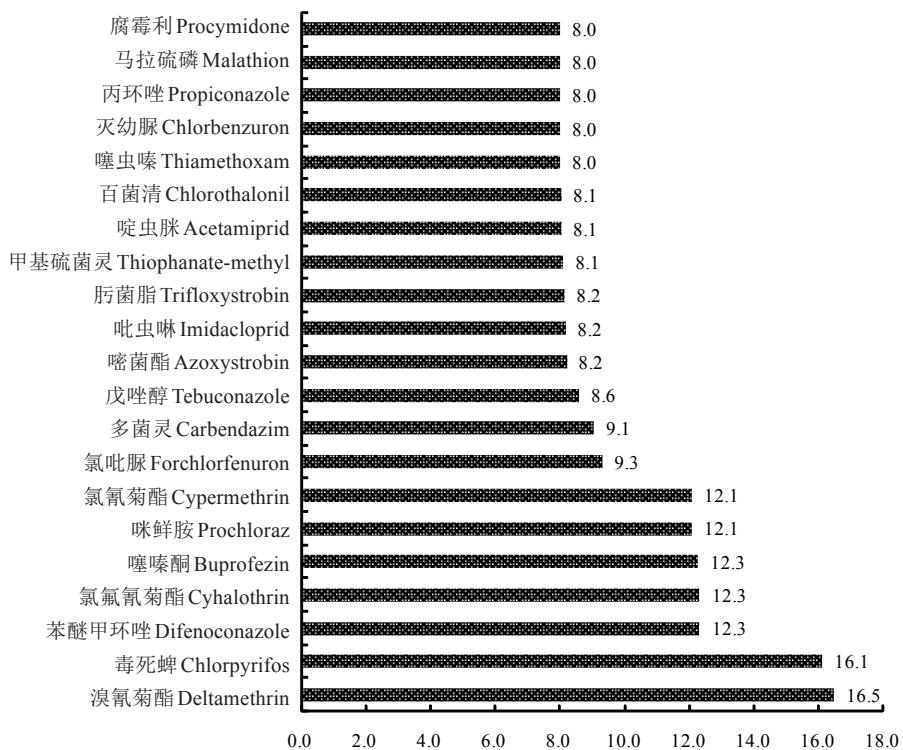


图1 猕猴桃中21种农药的残留风险排序

Fig. 1 Ranking of residue risk among the 21 pesticides applied to kiwifruit

氰菊酯、苯醚甲环唑5种农药风险得分S在12.1到12.4之间,腐霉利、氯吡脲等14种农药风险得分在8.0到9.3之间,即S<15,均为低风险农药;无高风险农药。根据公式(6)计算61个猕猴桃样品的农药残留风险指数(RI),并根据各农药残留风险指数(RI)将样品分为4类即高风险样品、中风险样品、低风险样品和极低风险样品,并对猕猴桃样品的农药残留风险指数进行统计。从图2中可以看出,61个猕猴桃样品中,共有28个即45.9%的样品处于极低风险区域(RI<5),21个即34.4%的样品处于低风险区域

(5≤RI<10),11个即18.0%的样品处于中风险区域(10≤RI<15)。农药残留风险得分是根据农药的毒性毒效、使用频率、残留水平、膳食量等指标来综合推算,由此说明,该主产区猕猴桃的质量状况相对较为安全,以中、低、极低风险样品为主,占98.4%。

2.4 农药最大残留限量值制定建议

检出的21种农药中,我国仅对多菌灵、啶虫脒、氯吡脲、溴氰菊酯、氯氟氰菊酯5种农药制定了猕猴桃或浆果及其他小型水果中的最大残留限量值(MRL)。利用猕猴桃日消费量(按照最大风险原则,取大份餐LP)、农药每日允许摄入量(ADI值)以及平均体重,根据公式(3)计算出猕猴桃中21种农药的最大残留限量估计值(eMRL)。从表4中可以看出,与eMRL相比,有限量的5种农药MRL值较严,如多菌灵eMRL是MRL的6.6倍,啶虫脒eMRL是MRL的3.8倍,氯氟氰菊酯eMRL是MRL的10.9倍,尤其是溴氰菊酯eMRL是MRL的21.9倍,氯吡脲eMRL是MRL的153倍。由于嘧菌酯、灭幼脲、马拉硫磷、腐霉利的eMRL均在10以上,因此暂时没有必要制定猕猴桃或浆果类果品中该4种农药的最大残留限量值。建议参考没有限量值的噻虫嗪、吡虫啉、甲基硫菌灵、戊唑醇、丙环唑、咪鲜胺、苯醚甲

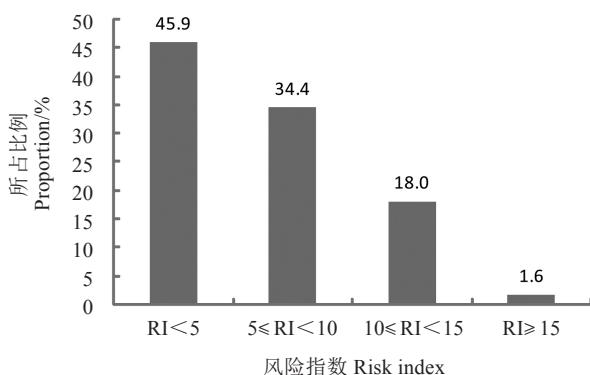


图2 猕猴桃样品中农药残留风险指数分布

Fig. 2 Distribution of pesticide residue risk index among kiwifruit samples

环唑、噻嗪酮、肟菌酯、毒死蜱、氯氟菊酯、百菌清共12种农药的最大残留限量估计值(eMRL),按照MRL比eMRL略宽、略严或相等且MRL≤SM(安全界限)的原则,结合毒理学数据来制定相应农药在猕猴桃树种上的最大残留限量值(MRL)。从表4中可以看出,所有农药的99.5百分位点残留值均显著低于最大残留限量(MRL)或最大残留限量估计值(eMRL),表明这些农药的最大残留限量或最大残留限量估计值是可行的,能够有效保护消费者健康。

表4 猕猴桃中21种农药的eMRL

Table 4 The eMRLs of 21 pesticides used in kiwifruit
(mg·kg⁻¹)

农药 Pesticide	ADI	SM	eMRL	MRL	P99.5
噻虫嗪 Thiamethoxam	0.08	41.98	8.747 9		0.021 5
多菌灵 Carbendazim	0.03	8.40	3.280 5	0.5	0.049 2
吡虫啉 Imidacloprid	0.06	33.58	6.561 0		0.124 5
啶虫脒 Acetamiprid	0.07	0.00	7.654 5	2(Berry)	0.005 5
甲基硫菌灵	0.08	16.79	8.747 9		0.555 9
Thiophanate-methyl					
氯吡脲 Forchlorfenuron	0.07	8.40	7.654 5	0.05	0.063 8
嘧菌酯 Azoxydstrobin	0.20	15.11	21.869 9		0.158 9
戊唑醇 Tebuconazole	0.03	8.40	3.280 5		0.070 4
灭幼脲 Chlorbenzuron	1.25	-	136.686 7		0.035 6
丙环唑 Propiconazole	0.07	25.19	7.654 5		0.009 4
咪鲜胺 Prochloraz	0.01	8.40	1.093 5		0.001 1
苯醚甲环唑	0.01	25.19	1.093 5		0.228 7
Difenconazole					
噻嗪酮 Buprofezin	0.01	56.25	0.984 1		0.032 5
肟菌酯 Trifloxystrobin	0.04	209.88	4.374 0		0.016 5
毒死蜱 Chlorpyrifos	0.01	8.40	1.093 5		0.205 4
溴氰菊酯 Deltamethrin	0.01	4.20	1.093 5	0.05	0.127 5
氯氟氰菊酯 Cypermethrin	0.02	3.36	2.187 0		0.107 4
马拉硫磷 Malathion	0.30	167.90	32.804 8		0.056 0
氯氟氰菊酯 Cyhalothrin	0.02	1.68	2.187 0	0.2(Berry)	0.354 7
百菌清 Chlorothalonil	0.02	50.37	2.187 0		0.086 4
腐霉利 Procymidone	0.10	8.40	10.934 9		1.638 0

3 讨 论

3.1 关于猕猴桃中农药风险水平

该主产区猕猴桃中66种农药中共检出21种,均为中等毒或低毒农药,绝大多数猕猴桃样品中农药残留量低于或远低于最大残留限量。另外借鉴英国兽药残留委员会兽药残留风险排序矩阵^[23],猕猴桃各检出农药的风险得分S以及各样品中农药残留风险指数(RI)的结果表明,检出的21种农药均为中风

险农药和低风险农药,仅溴氰菊酯和毒死蜱为中风险农药($15 \leq S < 20$),其余农药均为低风险农药($S \leq 15$)。61个猕猴桃样品中,45.9%的样品处于极低风险区域($RI \leq 5$),34.4%的样品处于低风险区域($5 \leq RI < 10$),18.0%的样品处于中风险区域($10 \leq RI < 15$)。因而,该主产区猕猴桃质量安全状况总体状况良好,以中、低、极低风险样品为主,占98.4%,相对较为安全。

3.2 关于猕猴桃急性和慢性膳食风险

利用农药毒理学数据(ADI值、ARfD值)、残留数据和猕猴桃消费数据对检出的21种进行风险评估结果表明,除了啶虫脒、灭幼脲无ARfD信息外,其余19种农药慢性膳食摄入风险(%ADI)和急性膳食摄入风险(%ARfD)均明显小于100%,说明猕猴桃各检出农药的急性和慢性膳食风险均在可以接受范围,并且风险都很低。笔者采用的农药残留风险评估方法是目前较为成熟也是应用较多的确定性评估方法,该方法简单易行且能够直接反映出膳食摄入风险水平,但评估结果较为保守,不能反映不同人群个体差异,因而有待于进一步进行基于不同年龄组人群的膳食摄入风险评估研究,同时开展农药残留、重金属、真菌毒素等多种污染物的混合污染联合毒性风险评估研究^[39]。通过揭示混合污染物联合毒性的相关规律,探索多种污染物混合污染的剂量-反应评估以及多参数累积暴露评估,从而提高果品中多污染物联合毒性风险评价预测的准确性和实用性。

3.3 关于猕猴桃中农药最大残留限量

目前在猕猴桃上有限量标准的农药较少,检出的21种农药中,我国GB 2763—2016仅对多菌灵、啶虫脒、氯吡脲、溴氰菊酯、氯氟氰菊酯5种农药制定了猕猴桃或浆果及其他小型水果中的最大残留限量值(MRL)^[29],无限量值农药占比76.2%,这就有待于今后不断完善标准。检出的21种农药中,除了多菌灵、啶虫脒、氯氟氰菊酯、溴氰菊酯和氯吡脲有MRL值以及嘧菌酯、灭幼脲、马拉硫磷、腐霉利4种农药没有必要制定MRL外,有必要对噻虫嗪、吡虫啉等12种农药制定MRL值。建议根据给出的最大残留限量估计值,按照MRL比eMRL略宽、略严或相等且MRL≤SM(安全界限)的原则,结合毒理学数据,制定没有限量值的噻虫嗪、吡虫啉共12种农药在猕猴桃树种上的最大残留限量值(MRL),以填补

我国果品质量安全限量标准的空白。

4 结 论

该主产区猕猴桃果实样品检出农药均为中等毒或低毒农药,且绝大多数猕猴桃样品中农药残留量低于或远低于最大残留限量。检出农药的其急性膳食摄入风险(%ARfD)、慢性膳食摄入风险(%ADI)均在可以接受范围内,98.4%的样品处于中、低或极低风险区域,总体来说该主产区猕猴桃质量安全状况良好。建议制定猕猴桃中噻虫嗪、吡虫啉等12种农药的MRLs。

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