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Dissipation behaviour, residue distribution and dietary risk assessment of tetraconazole and kresoxim-methyl in greenhouse strawberry via RRLC-QqQ-MS/MS technique

Xiaoxin Chen, Xueqi Fan, Yecheng Ma, Jiye Hu*

College of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

A R T I C L E I N F O

Chemical compounds studied in this article:
Tetraconazole (PubChem CID: 80277)
Kresoxim-methyl (PubChem CID: 6112114)

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A B S T R A C T

20% commercial suspension emulsion (SE) of (8% tetraconazole + 12% kresoxim-methyl), as a pre-registered product in China, was firstly investigated under Chinese greenhouse-field conditions. A MWCNTs-based QuEChERS method for simultaneous determination of tetraconazole and kresoxim-methyl in strawberry was developed and validated via RRLC-QqQ-MS/MS. On basis of this method, the dissipation behaviours, residue distributions and dietary risk probability of these fungicides in strawberry were further investigated for food safety. The dissipations of tetraconazole and kresoxim-methyl followed first-order kinetics with the half-lives of 8.0–18.2 days. The highest residues (HRs) of these fungicides in the supervised trials at the pre-harvest interval (PHI, 3 days) were below 0.8970 mg kg^{-1}. The total national estimated daily intake (NEDI) of tetraconazole and kresoxim-methy in strawberry at the PHI 3 day was 0.2784 mg and 0.4031 mg, respectively, based on Chinese dietary pattern and terminal residue distributions under good agricultural practices (GAP) conditions. The risk quotients (RQs) of tetraconazole and kresoxim-methy at PHI 3 days were below 82.7% and 1.6%, respectively, showing that the evaluated strawberry exhibited an acceptably low dietary risk to consumers. The current study could not only guide reasonable usage of the formulation, but also facilitate the setting of maximum residue limits (MRLs) of tetraconazole in strawberry.

1. Introduction

Strawberry fruits are one of the most popular and few purple vegetables due to its sweet flavor and preferred organoleptic properties (Samec et al., 2016). The consumption benefits of strawberry on cancer, cardiovascular, aging, senile dementia and other human diseases are documented (Sabera et al., 2016). Due to their huge commercial and economic significance, strawberries have been considered as the most studied berry from nutritional, genomic, or agronomic points of view (Giampieri et al., 2014). However, the strawberry quality and yield are severely reduced as a result of infestation by plant diseases and insect pests. To avoid this situation, various pesticides are frequently used in or on plant products. As a systemic fungicide, tetraconazole exhibits obvious effect on controlling strawberry powdery mildew. Nowadays, tetraconazole has been widely used in China etc. since its first introduction by ISAGRO SPA company. Kresoxim-methyl as a new strobilurin can inhibit mitochondrial respiration of fungi, thus prevent infection (Mercader et al., 2014). This fungicide shows special effects for powdery mildew of strawberry, muskmelon and cucumber. Due to the high-efficiency, low-toxicity and broad-spectrum, kresoxim-methyl has been widely used for chemical control of various harmful pests in many countries since its first introduction by BASF SE company. The chemical structures of tetraconazole and kresoxim-methyl are shown in Fig. 1(a, b).

As a pre-commercialized formulation, 20% tetraconazole and kresoxim-methyl suspension emulsion (SE) (Qingdao Hansen Biologic Science Co., Ltd) exhibits a significant effect on the control of strawberry powdery mildew. Presently, this new pesticide formulation is being registered by China, shortly afterwards, it may be widely popularized on a global scale. As is universally-known, food contamination issue, induced by potentially high/moderate levels of a number of environmental contaminants, has posed a threat to human health (Trabalon et al., 2016; Jacobs et al., 2016; Juan et al., 2017). Pesticides, as a kind of common environmental pollutants, have received

Abbreviations: ADI, acceptable daily intake; GAP, good agricultural practices; HRs, the highest residues; LODs, limits of detection; LOQs, limits of quantification; MRLs, maximum residue limits; MWCNTs, multi-walled carbon nanotubes; NEDI, national estimated daily intake; PHI, pre-harvest interval; RQ, risk quotient; RRLC-QqQ-MS/MS, rapid resolution liquid chromatography triples quadrupole tandem mass spectrometry; RSDs, relative standard deviations; SE, suspension emulsion; STMR, supervised trials median residue

* Corresponding author.
E-mail addresses: xiaoxinchen518@126.com (X. Chen), fanxueqi333@163.com (X. Fan), myc19930309@163.com (Y. Ma), jyhu@ustb.edu.cn (J. Hu).

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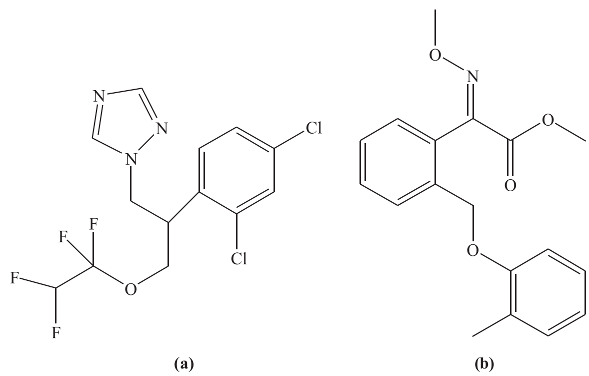

Fig. 1. Chemical structures of tetraconazole (a) and kresoxim-methyl (b).

increasing attention in recent years (Diop et al., 2016; Sabera et al., 2016). Hence, pesticides and toxicological metabolites residue in raw agricultural commodities (RACs) should be stringently monitored for food safety. According to GB2763-2016 and the JMPR report in 2001, the residue definitions of tetraconazole and kresoxim-methyl in plants only include parent compounds without any metabolites, so we only investigate tetraconazole and kresoxim-methyl parents in this study. Up to now, no literatures are available about dissipation behaviour and dietary risk assessment of tetraconazole and kresoxim-methyl in strawberry under Chinese good agricultural practices (GAP) conditions. Therefore, to evaluate the residue distribution and dietary risk probability of these fungicides will be an important aspect of food safety for Chinese authorities.

This study mainly aimed at (1): developing a sensitive and effective method for simultaneous determination of tetraconazole and kresoxim-methyl in strawberry samples; (2): investigating degradation behaviours and residue distributions of the pre-mixed suspension emulsion (SE) under greenhouse strawberry product conditions using the established method; and (3): assessing dietary risk probability of these fungicides in strawberry on basis of terminal residue data after both spraying three and four times at the recommended dosages.

2. Material and methods

2.1. Reagents and chemicals

Tetraconazole (99.0% purity) and kresoxim-methyl (99.2% purity) standards were provided by National Center for Quality Supervision and Testing of Pesticides (Shenyang, China). The HPLC-grade acetonitrile and formic acid were obtained from the Dikma Co., Ltd (Beijing, China). All of other reagents in the experiments were analytical-grade. N-(n-Propyl)ethylenediamine (PSA, 40 − 60 μm), multi-walled carbon nanotubes (MWCNTs) and syringe filter (nylon, 0.22 μm) were purchased from Bonna-Agela Technologies Venusil Technology Co., Ltd. (Tianjin, China). Formic acid solution (0.2%, v-v) was prepared before experiments. Standard stock solutions of tetraconazole (990 mg L^{-1}) and kresoxim-methyl (1000 mg L^{-1}) were prepared in HPLC-grade acetonitrile, respectively. Mixed standard working solutions with an equal concentration were serially diluted with HPLC-grade acetonitrile according to the concentrations of 2.5, 1, 0.5, 0.25, 0.1, 0.05 and 0.005 mg L^{-1}. All the solutions were stored at 4 °C.

2.2. Instrumental parameters

A rapid resolution liquid chromatography tandem triple quadrupled mass spectrometer (RRLC-QqQ-MS/MS) (Agilent 6420, USA) equipped with a reversed phase C18 column (50 mm × 3 mm I.D., 2.7 μm) was employed for liquid chromatography separation at 30 °C. An electro spray ionization interface was operated in positive ion mode (ESI^+). The sample injection volume was 5 μL. The mobile phase was the mixture of 0.2% formic acid solution (A) and acetonitrile (B) in volume ratio (v: v, 20:80) and the flow rate was 0.35 mL min^{-1}. The acquisition time was 2 min. The parameters of MS detection were as follows: gas temperature of 350 °C; gas flow rate of 11 L min^{-1}; nebulizer gas pressure of 45 psi; column temperature of 30 °C. The capillary voltages were controlled at 4000 V. The mode of multiple-reaction monitoring (MRM) was selected. The simultaneous quantification of tetraconazole and kresoxim-methyl were performed on basis of the acquisition parameters as listed in Table S1 and Fig. S1.

2.3. Sample preparation

In the QuEChERS method, the extract-solvent and cleanup-sorbent were optimized in advance. The doses of common cleanup sorbents (PSA, GCB, C18, florisil and MWCNTs) in dispersive solid-phase extraction (DSPE) procedure were explored, thus the optimal conditions were obtained. In brief, 5 g of the homogenised samples were weighed into 50 mL PTFE centrifuge tubes, to which 10 mL acetonitrile were added and vortexed for 1 min. Then, NaCl (1 g) and anhydrous $MgSO_4$ (4 g) were sequentially added and vortexed again for 1 min. The extracts were centrifuged for 3 min at 4000 rpm. 1.5 mL upper layer was transferred to a centrifuge tube with 150 mg anhydrous $MgSO_4$, 100 mg PSA and 10 mg multi-walled carbon nanotubes (MWCNTs). Subsequently, the centrifugal procedure was performed at 10,000 rpm for 3 min. The supernatant was filtered into an auto-sampler via with 0.22 μm syringe filter, and then it was analyzed using RRLC-QqQ-MS/MS analyzer. Simultaneously, the samples with no-pesticides were analyzed to use as blank control.

2.4. Recovery assay

The mixed standard solutions of tetraconazole and kresoxim-methyl were used to fortify control strawberry at the appropriate concentrations of 0.005, 0.1, 5 mg kg^{-1}. These samples were extracted and purified according to the above procedure. Five parallel treatments for each fortified level were carried out. The blank control was also analyzed to calibrate the interference from strawberry matrix.

2.5. Field trials

The field trials of degradation dynamic and terminal residue were conducted at two representative locations: Beijing (116.46°E, 39.92°N, warm temperate and semi-humid continental monsoon climate, north of China), Laiyang city of Shandong province (120.9°E, 36.97°N, warm temperate regions, semiarid continental monsoon climate, east of China). The field experiments were designed according to NY/T 788–2004 (Guideline on Pesticide Residue Trials) issued by Ministry of Agriculture, P. R. China. There were five experimental plots with 30 m^2 and three replications for each treatment. A buffer zone with 0.5 m width was used to separate these plots with different treatments. The characteristics of soils used for field trials at the two locations were as follows: Beijing soil belongs to sandy loam type, with an organic matter of 2.7%, pH value of 7.32 and cation exchange capacity (CEC) of 29.7 cmol kg^{-1}. The Shandong soil was clay loam with the organic matter of 3.9%, pH of 6.73, CEC of 16.7 cmol kg^{-1}.

To study the dissipation kinetics of tetraconazole and kresoxim-methyl in strawberry, a commercial suspension emulsion (SE) of (8% tetraconazole + 12% kresoxim-methyl) was diluted with water and sprayed on blank strawberry at a dosage of 225 g active ingredient per ha (g a.i. ha^{-1}) (1.5 times of recommended high dosage). To obtain blank samples, a separate plot with the same size and no-pesticide application was treated with clear water. The representative strawberry samples (2 kg) were collected randomly from each plot at different time intervals (0, 1, 3, 5, 7, 14, 21 and 30 days) from the experimental strawberry plots. These samples were cut into 1 cm squares by food cutter, and then they were maintained at −20 °C until analyzed.

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