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Residue Monitoring and Dietary Risk Evaluation of Fungicide Propiconazole in Leafy Vegetables under Greenhouse Conditions

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Abstract

Residue monitoring of propiconazole (PCZ) in cabbage, shallot, and spinach was conducted under multi-trial greenhouse conditions. This study aimed to understand the fate of the applied fungicide in these vegetables. Furthermore, the associated health risk of PCZ in leafy vegetables was assessed through dietary risk assessment. Commercially available PCZ (22% suspension concentrate) was administered thrice according to the OECD fungicide application interval guideline. The plant samples were extracted using a slightly modified QuEChERS technique and analyzed using gas chromatography-tandem mass spectrometry. The average PCZ recovery was between 84.5% and 117.6%, with a <5% coefficient of variance. The dissipation of PCZ residue in cabbage, shallot, and spinach after 14 days was 96%, 90%, and 99%, respectively, with half-lives of <5 days. Meanwhile, dietary risk assessments of PCZ residues in the studied vegetables

using the risk quotient (RQ) were significant < 100 (RQ < 100). Thus, the population groups considered in this study were not at substantial risk from consuming leafy vegetables sprayed with PCZ following critical, good agricultural practices.

Key words: Dietary risk assessment, Leafy vegetables, Maximum residue limits, Propiconazole, Residue monitoring

Fig. 1. Chemical structure of propiconazole.

Introduction

Vegetables are an important component of human diet because they supply vital vitamins, dietary fiber, minerals in the form of electrolytes, and phytochemicals that help prevent chronic diseases. The perceived health and nutritional benefits of leafy vegetables has led to increased consumption of fresh and unprocessed vegetables in the Republic of Korea [1,2]. Pesticides are used during different physiological growth periods following the safety guidelines in Korea for the effective control of vegetable pests and incidences of diseases. However, the excessive use and inappropriate dosing of unregistered pesticides on crops may pose adverse health impacts on consumers and disrupt the natural ecosystems of microflorae and faunae [3,4]. To prevent the consumption of crops with high pesticide concentrations, standards must be established to ensure regular monitoring of residue concentrations in agricultural products. Therefore, various countries have implemented maximum residue limits (MRLs) for agricultural food products. For example, the maximum residue limit set for the pesticide in Europe is 0.05 mg/kg in leafy greens, 0.05 mg kg^{-1} in Japan [5], and 0.02 mg/kg for pineapple in China [6]. Hence, residue concentrations and their associated risks have become an important aspect of monitoring and safety assessment of edible crops, especially vegetables.

Propiconazole (PCZ) is a systemic, broad-range triazole fungicide that is effective against a variety of fungal pathogens [7,8]. The mechanism of action of PCZ involves the inhibition of ergosterol anabolism in fungi, which prevents spore formation [9]. This inhibitory effect is attributed to the five-membered heterocyclic structure of PCZ, which contains three nitrogen atoms, as shown in Fig. 1. However, triazole fungicides, including PCZ, are also known to have endocrine-disrupting effects, which pose substantial hazards
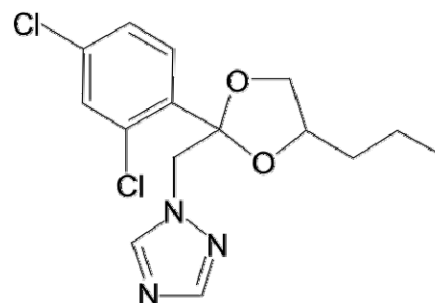
to human health. PCZ is capable of causing blood imbalance and various dysfunctions in the nervous system [5,10]. Despite these concerns, several studies have reported the conventional use of PCZ for preventing fungal diseases in fruit, cash crops, and staple crops [11,12].

Although propiconazole is registered for use on crops according to standard protocol, previous studies have primarily focused on monitoring its concentrations in livestock samples [13,14]. However, research on PCZ related food safety issues in the Republic of Korea is limited. Hence, the specific goals of this study were to: (1) apply a modified AOAC QuEChERS analysis method to determine PCZ residue in commonly consumed leafy vegetables, such as cabbage, shallot, and spinach, after foliar application under greenhouse conditions; (2) determine the residue concentrations and biological half-lives of PCZ in these leafy vegetables; and (3) evaluate the potential dietary risks associated with consuming leafy vegetables treated with PCZ among different population groups. Simultaneously, this study serves as a basis for establishing MRLs, regulating the use of PCZ under field conditions, providing data for in-depth studies on the safe use of PCZ, and predicting dissipation dynamics of PCZ in crops with similar traits to those studied in this research.

Materials and Methods

Chemicals and reagents

Field experiments were conducted using commercially available propiconazole (PCZ) purchased from NongHyup Chemical Co., Ltd., Republic of Korea, Youngil Best (22% SC). The PCZ analytical standard (99.7% purity) was acquired from Sigma-Aldrich Co. (USA). Formic acid was provided by Duksan Pharmaceuticals Company, Republic of Korea, while sodium

chloride (general reagent grade) was supplied by Jun-sei Chemical Company, Japan. Acetonitrile (MeCN), methanol, and water (H_2O) (all HPLC grade) were procured from Honeywell Burdick and Jackson, Inc. (USA). QuEChERS buffer salts, magnesium sulfate, and primary secondary amines were provided by Pheno-menex Co., USA. PCZ stock solution (400 mg/L) was dissolved in HPLC-grade acetone.

Greenhouse trial design

A multiregional greenhouse field trial was conduc-ted at three locations, including Gumi-si, (36.24 °N, 128.29 °E), Yesan-gun (36.73 °N, 126.79 °E), Waegwan-eup (35.90 °N, 128.40 °E) in the Republic of Korea, for spinach, shallot, and cabbage, respectively. Following the OECD field guidelines [15], each greenhouse was partitioned into plots of 2 m × 15 m in accordance with the preharvest treatment intervals, which corre-sponded with the fungicide application time and a 1.5 m buffer zone was created between treated plants to avoid cross-contamination. A commercial-grade for-mulation of PCZ was applied at a dosage of 22 g a.i./ 10 acres employing an electric knapsack sprayer cali-brated at 1,500 mL/min. Control plots were designed based on the layout of the treatment plots without fungicide application.

Sample preparation, extraction, and clean-up procedure

Freeze-dried leafy vegetable samples were evenly homogenized using a plug-in blender (12,000 rpm) and preserved at -20°C for further analysis. The AOAC QuEChERS analysis method was slightly modified in terms of sample weight to develop an optimized ana-lytical method. Briefly, 10 g of triturated leafy green samples were weighed in a 50 mL high-clarity SPL-conical tube. Following the addition of 10 mL of 1% acetic acid in acetonitrile, the mixture was subjected to agitation using a multitube Collomix shaker at 3,600 rpm for 2 minutes. Subsequently, 1.5 g of NaOAc and 6 g of anhydrous $MgSO_4$ were added to the extract, followed by vigorous shaking for 5 min and centrifu-gation at 2898 rcf for 4 min. For the dispersive clean-up procedure, 1 mL aliquot of supernatant fraction was pipetted into microfuge tubes containing 25 mg PSA and 150 mg anhydrous $MgSO_4$. These samples were centrifuged for 5 min at 10,000 rpm and filtered using a 0.2 μm PVDF membrane syringe.

Instrument characterization

Characterization was conducted using a GC-MS-TQ 8050 Triple Quadrupole Gas Chromatograph Mass Spectrometer (Shimadzu Corp., Kyoto, Japan). A ZB-5MS plus (Phenomenex Co., Torrance, CA, USA; 30 m capillary column × 0.25 mm internal diameter × 0.25 μm film thickness) gas chromatograph was used for PCZ separation and identification. The column oven temperature was increased from 90°C to 120°C and ultimately to 300°C corresponding to the flow rates of 0°C min^{-1}, 220°C min^{-1}, and 80°C min^{-1} and maintained for 3 min. The injector, interface, and ion source tem-peratures were selected based on the maximum per-formance during calibration. The quad 2 collision gas was Argon, while the carrier gas was Helium. GC-MS/MS was operated at a column flow rate (constant) of 1.5 mL/min and 1 μL injected in (splitless mode). The MS detector voltage was 0.5 kV, with a collision pres-sure of 1.5 mTorr and an electron ionizing voltage of -70 eV.

Method validation

Analytical methods were assessed using a matrix-matched calibration curve. The standard calibration curve was obtained from chromatogram peak areas at concentrations varying from 0.005 to 0.2 mg/L. Stock solutions and blank were uniformly assessed for spe-cificity. Following the established recovery guidelines of the ministry of food and drug safety (MFDS), the control samples for each leafy vegetable were fortified with a standard PCZ solution of known concentrations. This was done in quintuplicate for both the method quantification limit (MQL) and 10 times the MQL.

Half-life and risk assessment calculations

The dissipation kinetics of PCZ was analyzed using the first-order model as expressed in Eq. 1.

$$C_t = C_o \, e^{-kt} \tag{1}$$

where C_t is the concentration in (mg/kg) after a specific duration t and C_o is the initial concentration (mg/kg).

The PCZ half-life was determined based on K (dis-sipation rate constant) as expressed in Eq. 2.

$$t_{1/2} = \ln 2 \, / \, k \tag{2}$$

where $t_{1/2}$ is half-life (DT_{50} estimated in days)

Additionally, dietary risk evaluation was conducted to estimate the risk quotient (RQ) of PCZ [16]. RQ ≥ 100 indicates high dietary risk and RQ ≤ 100 indicates negligible or no dietary risk of the applied fungicide. The national estimated daily intake (NEDI) and RQ were calculated as shown in Eq. 3 and Eq. 4.

$$NEDI = \frac{\text{Mean residue concentration (mg/kg)} \times \text{average food intake (kg)}}{\text{body weight (kg)}} \quad (3)$$

$$RQ = \frac{NEDI \, (\text{mg/kg bw})}{ADI \, (\text{mg/kg bw})} \times 100 \quad (4)$$

where ADI is the acceptable daily intake of PCZ.

Statical analysis

The GC-MS/MS data were evaluated using Shimadzu LabSolutions GCMS Version 5.4. The MS Excel Solve add-in and SigmaPlot (version 12, Systat Software Inc.) were used for data visualization and presentations.

Results and Discussion

Analytical method optimization

The percentage recovery range, correlation coefficients, MDA, and the MQL were used to validate the efficiency of the proposed analytical method. To determine the linearity and correlation coefficients, standard solvent solutions were compared with matrix-matched standard solutions. The correlation coefficients obtained in this study agreed well with those obtained in pre-

vious investigations with values ≥ 0.9995 for PCZ in the three analyzed crop samples which indicates good linearity [8,16]. The coefficient of linearity (R^2), calibration curve equation, and the quantification limit for PCZ are presented in Table 1 MDA (0.1 ng) and MQL (0.01 mg/kg) used in this investigation indicated the precision and reliability of the analytical procedure. Moreover, the average percent recovery (%) was obtained by spiking a standard solution of PCZ at MQL and 10×MQL in the control samples.

The percentage recovery data in (Table 1) corroborates the accuracy of the PCZ analytical procedures. Particularly, the average recovery (%) for PCZ ranged from 107.0 to 115.9 in cabbage, 94.1 to 114.1 in shallot, and from 96.3 to 112.7 in spinach. Thus, the accuracy was validated to be within the acceptable recovery value of 70–120% [17, 18]. The PCZ retention time (rt) in fortified and untreated matrices exhibited no chromatographic interference, indicating good sensitivity of the developed method. Thus, the percentage relative standard deviation (RSD), which indicates precision, was between 0.7% and 2.6%, was within the acceptable RSD percentage (<20%).

Similar microclimate-controlled studies have analyzed the validation of various analytical techniques and the QuEChERS method for detecting fungicides in leafy vegetables and fruits having high moisture content [19,20]. Many modifications were done on original QuEChERS to achieve better extraction of pesticdes. AOAC QuEChERS resembles the original QuEChERS but a buffer salt (sodium acetate) is changed to maintain the pH during the extraction mainly with sample which improved the recovery. Previous studies on the

Table 1. Method validation of the propiconazole in samples of cabbage, spinach, and shallot (linearity of calibration curves, recovery)

Crop	Calibration equation ($y^{a)} = ax^{b)} + b$)	R^2	Fortification level (mg/kg)	Recovery (%)					$SD^{c)}$
				1	2	3	4	5	
Cabbage	y = 896,684.463x + 1,256.996	0.9995	0.01	109.8	110.2	104.6	104.5	106.1	2.8
			0.1	111.7	110.7	112.6	112.7	113.7	1.1
			2.0	115.5	113.2	116.4	116.7	117.6	1.7
Shallot	y = 89,349.129x + 1,955.725	0.9998	0.01	93.7	95.1	93.1	93.2	95.8	1.2
			0.1	113.5	113.3	114.0	114.9	115.0	0.8
			2.0	101.2	96.0	97.8	98.2	99.2	1.9
Spinach	y = 117,990.047x + 2,029.136	0.9996	0.01	94.5	98.9	97.8	93.8	96.4	2.2
			0.1	114.4	113.8	111.7	112.5	110.8	1.5
			6.0	106.5	105.8	108.5	102.1	105.9	2.3

a) Peak area in MS/MS spectrum, b) Residue of pesticides in samples (ng), c) Standard Deviation

residue characteristics of PCZ [4,8,21] in celery, grape, wheat straw, and mango validated quality control in terms of linearity, lowest detectable concentrations, quantification limits, and precision [12,16]. Similarly, a few previous studies [22,23] validated the analytical method for the identification of conazole fungicides in pomegranate. Hence, this study presents an adaptable technique and a method validation that is compatible with previous investigations with respect to the assessment of PCZ in fruits and vegetables having acceptable analytical parameters.

Dissipation of propiconazole (PCZ) in leafy vegetables

The concentration of PCZ residue in the control samples was below the established MQL (0.01 mg/kg). Conversely, the amount of residue in the treated samples was calculated by applying the first-order rate equation [3]. The regression mathematical expressions for degradation were $C_t = 1.9633e^{-0.234x}$, $C_t = 4.2858e^{-0.335x}$, and $C_t = 1.4182e^{-0.155x}$, with correlation coefficients of 0.998, 0.993, and 0.970 in cabbage, spinach, and shallot respectively. PCZ residue levels decreased as the duration of fungicide sampling increased, as shown in Table 3. The dissipation pattern of PCZ was comparable across the analyzed crops. Notably, PCZ dissipation in cabbage, shallot, and spinach was as high as 60% 7 days after application. However, after the sampling interval (i.e., 21-14 days after treatment), >95% of PCZ residue had degraded in cabbage and spinach while PCZ residue concentration in shallot samples had dissipated by ~90%. These findings agree with those reported in a previous study on PCZ degradation in various fruits, crops, and vegetables [9,12, 16,24]. For example, PCZ degraded by >87% in grapes and mangos 3 days post-application and by >97% after 10 days [4]. In comparison, a degradation of >50% was observed in celery and <50% in onions, 7 days after application, suggesting rapid PCZ dissipation in the analyzed leafy greens [16]. In other studies, PCZ dissipated by >92% in pomegranate 30 days after application and by >95% in wheat straw 28 days after application [12,22].

In general, the dissipation of pesticides in crops during their growth stages is influenced by numerous variables, including initial pesticide concentration, pesticide formulation, rate of application, plant species, environmental factors, and bio-and photo-transformation [25-27]. Several greenhouse studies on residue dis-sipation have demonstrated that prevailing environmental conditions, such as wind velocity, sunshine hours, and temperature plays a key role in fungicide dissipation [1,3,28]. Xu et al. [30] highlighted that variations in wind velocity across different study regions affected the decrease in residual concentration of PCZ in banana foliage. Herein, although PCZ was applied uniformly across the different greenhouse locations, the rate of dissipation was found to be faster in spinach followed by that in cabbage and shallot. Hence, the result of this study suggests that the dissipation rate of PCZ can vary based on crop morphology and ambient conditions.

Initial deposition and In-plant comparative assessment of propiconazole (PCZ)

The in-plant assessment and the initial residue amounts were evaluated to understand the fungicide residue behavior in the environment and analyzed crops. The initial residue concentration forms an important basis for establishing MRL for crops, and it corresponds to the residue level detectable after two hours of fungicide application [15,30]. The residue concentration of PCZ was found to be highest on day 0, ranging from 1.97-2.96, 1.46-1.60, and 5.82-6.26 mg/kg in cabbage, shallot, and spinach, respectively. In shallot, the initial deposition of PCZ (1.53 mg/kg) was relatively lower than that observed in cabbage and spinach (2.05 and 6.11 mg/kg respectively), as shown in Table 2. This is because of the high specific surface area, coupled with the vertical, deep, and cylinder-shaped leaf architecture of shallot compared to the broad, horizontal, and wide leaf architecture of spinach and cabbage [31]. A previous study conducted using spirotetramat recorded approximately three times the initial amount of the pesticide in Korean cabbage samples at 10.03 mg/kg as compared to that in shallot samples at 3.29 mg/kg [17].

Similarly, studies based on residual amount of fungicide cyazofamid sprayed on Korean cabbage reported an initial concentration of >9 mg/kg at day 0 [15]. Opolot et al. [19] reported the initial residue amount of sulfoxaflor to be greater in spinach than in Korean cabbage. A recent scientific report by [30] indicated that the initial concentration of picarbutrazox on cabbage was found to reach a maximum value of 13.72 mg/kg. The findings of this study are consistent with previous reports indicating that several factors, including evapotranspiration, plant metabolism, photolysis,

Table 2. Mean residue concentrations of propiconazole in cabbage, shallot, and spinach samples in varying preharvest interval (PHIs)

Crops	Preharvest interval (PHI)	Mean residue amounts (mg/kg)			SD[a)]
		1	2	3	
Cabbage	Control	<MQL[b)]			-
	0	0.08	0.07	0.07	0.01
	3	0.31	0.32	0.33	0.01
	7	1.03	1.00	1.02	0.02
	14	1.97	2.01	2.16	0.10
Shallot	Control	<MQL			-
	0	0.17	0.14	0.16	0.02
	3	0.55	0.54	0.51	0.02
	7	0.77	0.75	0.77	0.01
	14	1.60	1.52	1.45	0.07
Spinach	Control	<MQL			-
	0	0.07	0.07	0.07	0.00
	3	0.11	0.11	0.10	0.00
	7	2.31	2.42	2.21	0.11
	14	5.82	6.26	6.24	0.25

[a)] Standard Deviation, [b)] Method Quantification Limits

crop growth rate, plant pore size, and crop sizes, can affect the initial deposition of pesticide residues in plants [1,22,32]. The weather conditions during the study, reveal a comparatively lower average temperature and high relative humidity for shallot greenhouse compared to those for cabbage and spinach. This could be a potential factor contributing to the delayed dissipation rate observed in shallot samples, as shown in Fig. 2. Currently, MRLs have not been set for the leafy vegetables studied in this research. Hence, the findings from this study can offer guidance and serve as a baseline for setting tolerable residue levels of PCZ in leafy vegetables.
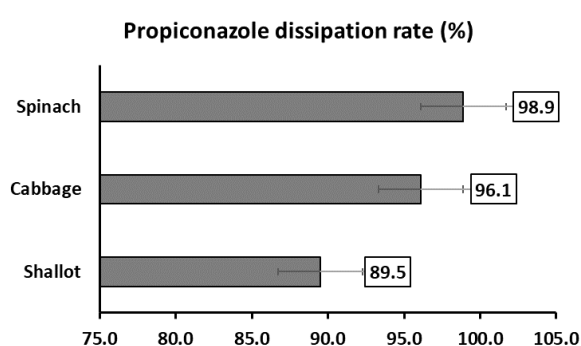
Biological half-lives of propiconazole (PCZ) in leafy vegetables

The half-life period of PCZ was less than 5 days in the crops studied herein. Particularly, the half-life periods of PCZ in cabbage, shallot, and spinach were 2.96, 4.47, and 2.06 days, respectively, as shown in Table 3. The half-live (DT_{50}) values obtained in this study are shorter than those observed in Jonagold apple, pomegranate, banana, and celery but longer than those in grapes and mango. For instance, the DT_{50} of PCZ was found to be 13 days in Jonagold apples, 7.9-8.2 days in pomegranate, 13.9-23.3 days in bananas, 6.1 days in onions, and 8.7 days in celery [17,30]. Zhang et al. [12] reported a half-life of 5.1-6.9 days in wheat straw. In another study, the DT_{50} of PCZ was observed to be 1.24 days in grapes and 1.19 days in mangoes in field conditions [4]. Environmental factors, fungicide formulations, application rate, and crop species are among the various factors that can affect the rate of

Propiconazole dissipation rate (%)

Fig. 2. Comparison of the rate of dissipation of propiconazole in spinach, cabbage, and shallot samples.

Table 3. Residue equations, half-lives, and correlation coefficient of propiconazole in leafy vegetables

Crop	Residue equation	Half-life (days)	R^2
Cabbage	$C_t = 1.9633e^{-0.234x}$	2.96	0.998
Shallot	$C_t = 1.4182e^{-0.155x}$	4.47	0.970
Spinach	$C_t = 4.2858e^{-0.335x}$	2.06	0.993

Table 4. Estimated daily intake and the associated risk quotient of propiconazole in leafy vegetables among various population groups

Crop	11 kg		30 kg		67 kg	
	EDI	RQ-infant (%)	EDI	RQ-Child (%)	NEDI	RQ-Adult (%)
Cabbage	0.00079	1.1343	0.00120	1.7181	0.00080	1.1387
Shallot	0.00024	0.3360	0.00015	0.2108	0.00012	0.1661
Spinach	0.00057	0.8203	0.00025	0.3607	0.00015	0.2162

degradation of pesticide residues in vegetables [33,34]. In this study, the differences in half-life values were attributed to variations in the fungicide metabolism capacities of the crops and the prevailing environmental conditions in the experimental plots [35]. Thus, growth conditions, pesticide formulations, and the nature of the crops being studied should be the key considerations in the studies related to the half-lives of pesticides for specific crop species.

Dietary risk assessment of propiconazole (PCZ) in leafy vegetables

Consumers might face substantial health risks from the persistent consumption of fruits and vegetables with high levels of pesticide residues because these residues are often not eliminated even with washing. To evaluate this risk, the dietary exposure of PCZ was assessed against the ADI values established by the Korean regulatory authority (MFDS) for PCZ (0.07 mg/kg/body weight/day). The RQ in this study was evaluated using data from the Korean Health Industry Development Institute. Data regarding the population of adults (67 kg), children (30 kg), and infants (11 kg) used in this study were obtained from Korea Statistical Information Service. The NEDI and health RQ percentages of PCZ in cabbage, spinach, and shallot across the analyzed population groups are presented in Table 4. Similarly, we found that the estimated daily intake values were lower than the ADI values, which were influenced by the difference in dietary habits among the population groups. Conversely, the RQ percentage values obtained in this study agree with a previous PCZ research conducted on Chinese vegetables with the percentage risk assessment values in the range of 0.0083-3.125 [16]. Table 3 also indicates that RQ values were less than 100% in the three population groups, suggesting that there is negligible dietary risk associated with the consumption of PCZ residues in cabbage, spinach, and shallot.

Conclusion

This study conducted a comprehensive residue determination of PCZ in commonly consumed leafy vegetables using a modified AOAC QuEChERS method coupled with GC-MS/MS. The established MQL was 0.01 mg kg^{-1} in all analyzed samples. Overall, the PCZ residue concentration and biological half-lives were found to be in the following order: shallot > cabbage > spinach, 21-14 days after application. Dietary risk assessment was conducted using the NEDI, ADI, RQ, and average body weight values indicated that no significant risk was identified for the three population groups (children, infants, and adults) with the consumption of leafy vegetables treated with PCZ using good agricultural practices and good experimental field practices. Hence, regular research on the monitoring of pesticides to facilitate the formulation of appropriate field safety guidelines and establish the maximum tolerable residue concentration limits in specific crops under diverse growing conditions is necessary to ensure consumer safety.

Note

The authors declare no conflict of interest.

Acknowledgement

References

1. Sardar SW, Byeon GD, Choi JY, Ham HJ, Ishag AESA, Hur JH (2022) Residual characteristics and safety assessment of the insecticides spiromesifen and chromafenozide in lettuce and perilla. Scientific Reports, 12(1), 4675.

https://doi.org/10.1038/s41598-022-08532-2.

2. Yi YJ, Joung HJ, Kum JY, Hwang IS, Kim MS (2020) Pesticide residues in vegetables and risk assessment for consumers in Korea during 2010-2014. Food Additives & Contaminants: Part A, 37(8), 1300-1313. https://doi.org/10.1080/19440049.2020.1769198.

3. Hwang JI, Kim HY, Lee SH, Kwak SY, Zimmerman AR, Kim JE (2018) Improved dissipation kinetic model to estimate permissible pre-harvest residue levels of pesticides in apples. Environmental Monitoring and Assessment, 190, 1-11. https://doi.org/10.1007/s10661-018-6819-8.

4. Soliman AS, Helmy RM, Nasr IN, Abbas MS, Mahmoud HA, Jiang W (2017) Behavior of thiophanate methyl and propiconazole in grape and mango fruits under the egyptian field conditions. Bulletin of Environmental Contamination and Toxicology, 98, 720-725. https://doi.org/10.1007/s00128-017-2066-x.

5. Wang C, Wang Y, Wang R, Yan J, Lv Y, Li A, Gao J (2017) Dissipation kinetics, residues and risk assessment of propiconazole and azoxystrobin in ginseng and soil. International Journal of Environmental Analytical Chemistry, 97(1), 1-13. https://doi.org/10.1080/03067319.2016.1272678.

6. Li KL, Chen WY, Zhang M, Luo XW, Liu Y, Zhang DY, Chen A (2022) Monitoring residue levels and dietary risk assessment of thiamethoxam and its metabolite clothianidin for Chinese consumption of Chinese kale. Journal of the Science of Food and Agriculture, 102(1), 417–424. https://doi.org/10.1002/jsfa.11371.

7. Satapute P, Kamble MV, Adhikari SS, Jogaiah S (2019) Influence of triazole pesticides on tillage soil microbial populations and metabolic changes. Science of the Total Environment, 651, 2334–2344. https://doi.org/10.1016/j.scitotenv.2018.10.099.

8. Tang S, Meng X, Wang F, Lin Q, Feng T, Hu D, Zhang Y (2022) Four propiconazole stereoisomers: Stereoselective bioactivity, separation via liquid chromatography-tandem mass spectrometry, and dissipation in banana leaves. Journal of Agricultural and Food Chemistry, 70(3), 877-886. https://doi.org/10.1021/acs.jafc.1c06253.

9. Hamed SM, Al-Nuaemi IJ, Korany SM, Alsherif EA, Mohamed HS, Abdelgawad H (2022) Hazard assessment and environmental fate of propiconazole degradation by microalgae: Differential tolerance, antioxidant and detoxification pathway. Journal of Environmental Chemical Engineering, 10(4), 108170. https://doi.org/10.1016/j.jece.2022.108170.

10. Li J, Ding Y, Chen H, Sun W, Huang Y, Liu F, Wang M, Hua X (2022) Development of an indirect competitive enzyme-linked immunosorbent assay for propiconazole based on monoclonal antibody. Food Control, 134, 108751. https://doi.org/10.1016/j.foodcont.2021.108751.

11. Abdallah OI, Alrasheed AM, Al-Mundarij AA, Omar AF, Alhewairini SS, Al-Jamhan KA (2021) Levels of residues and dietary risk assessment of the fungicides myclobutanil, penconazole, tebuconazole, and triadimenol in squash. Biomedical Chromatography, 35(8), e5126. https://doi.org/10.1002/bmc.5126.

12. Zhang Z, Jiang W, Jian Q, Song W, Zheng Z, Wang D, Liu X (2015) Residues and dissipation kinetics of triazole fungicides difenoconazole and propiconazole in wheat and soil in Chinese fields. Food Chemistry, 168, 396-403. https://doi.org/10.1016/j.foodchem.2014.07.087.

13. Jeong JY, Kim B, Ji SY, Baek YC, Kim M, Park SH, Kim KH, Oh SI, Kim EJ, Jung HJ (2021) Effect of pesticide residue in muscle and fat tissue of pigs treated with propiconazole. Food Science of Animal Resources, 41(6), 1022. https://doi.org/10.5851/kosfa.2021.e533.

14. Lee SH, Kwak SY, Sarker A, Moon JK, Kim JE (2022) Optimization of a multi-residue analytical method during determination of pesticides in meat products by GC-MS/MS. Foods, 11(19), 2930. https://doi.org/10.3390/foods11192930.

15. Sarker A, Lee SH, Kwak SY, Nam AJ, Kim HJ, Kim JE (2020) Residue monitoring and risk assessment of cyazofamid and its metabolite in Korean cabbage under greenhouse conditions. Bulletin of Environmental Contamination and Toxicology, 105, 595-601. https://doi.org/10.1007/s00128-020-02972-0.

16. Bai A, Chen A, Chen W, Luo X, Liu S, Zhang M, Liu Y, Zhang D (2021) Study on degradation behaviour, residue distribution, and dietary risk assessment of propiconazole in celery and onion under field application. Journal of the Science of Food and Agriculture, 101(5), 1998-2005. https://doi.org/10.1002/jsfa.10817.

17. Nandi R, Kwak SY, Lee SH, Sarker A, Kim HJ, Lee DJ, Heo YJ, Kyung KS, Kim JE (2022) Dissipation characteristics of spirotetramat and its metabolites in two phenotypically different Korean vegetables under greenhouse conditions. Food Additives & Contaminants: Part A, 39(5), 964-976. https://doi.org/10.1080/19440049.2022.2046293.

18. Wu S, Zhang H, Zheng K, Meng B, Wang F, Cui Y, Zeng S, Zhang K, Hu D (2018) Simultaneous determination and method validation of difenoconazole, propiconazole and pyraclostrobin in pepper and soil by LC-MS/MS in field trial samples from three provinces, China. Biomedical Chromatography, 32(2), e4052. https://doi.org/10.1002/bmc.4052.

19. Opolot M, Lee SH, Kwak SY, Sarker A, Cho SC, Kim HJ, Jeong HR, Kim JE (2018) Dissipation patterns of insecticide sulfoxaflor in spinach and Korean cabbage. The Korean Journal of Pesticide Science, 22(4), 316-326. https://doi.org/10.7585/kjps.2018.22.4.316.

20. Tankiewicz M, Berg A (2022) Improvement of the QuEChERS method coupled with GC-MS/MS for the determination of pesticide residues in fresh fruit and vegetables. Microchemical Journal, 181, 107794. https://doi.org/10.1016/J.MICROC.2022.107794.

21. Cheng Y, Zheng Y, Dong F, Li J, Zhang Y, Sun S, Li N, Cui X, Wang Y, Pan X, Zhang W (2017) Stereoselective analysis and dissipation of propiconazole in wheat, grapes, and soil by supercritical fluid chromatography－tandem mass spectrometry. Journal of Agricultural and Food Chemistry, 65(1), 234-243. https://doi.org/10.1021/acs.jafc.6b04623

22. Mohapatra S (2016) Dynamics of difenoconazole and propiconazole residues on pomegranate over 2 years under field conditions. Environmental Science and Pollution Research, 23, 5795-5806. https://doi.org/10.1007/s11356-015-5785-8.

23. Wayment DG, Ledet HJ, Torres KA, White PM (2021) Soil dissipation of sugarcane billet seed treatment fungicides and insecticide using QuEChERS and HPLC. Journal of Environmental Science and Health, Part B, 56(2), 188-196. https://doi.org/10.1080/03601234.2020.1858685.

24. Munitz MS, Medina MB, Montti MIT (2017) Development and validation of an SPME-GC method for a degradation kinetics study of propiconazole I, propiconazole II and tebuconazole in blueberries in Concordia, the main production area of Argentina. Food Additives & Contaminants: Part A, 34(5), 793-799. https://doi.org/10.1080/19440049.2017.1301682.

25. Fantke P, Juraske R (2013) Variability of pesticide dissipation half-lives in plants. Environmental Science & Technology, 47(8), 3548-3562. https://doi.org/10.1021/es303525x.

26. Klink H, Verreet JA, Hasler M, Birr T (2021) Will triazoles still be of importance in disease control of Zymoseptoria tritici in the future?. Agronomy, 11(5), 933. https://doi.org/10.3390/agronomy11050933.

27. Kwak SY, Lee SH, Jeong HR, Nam AJ, Sarker A, Kim HY, Lim CU, Cho HJ, Kim JE (2019) Variation of pesticide residues in strawberries by washing and boiling processes. Korean Journal of Environmental Agriculture, 38(4), 281-290. https://doi.org/10.5338/kjea.2019.38.4.38.

28. Kwak SY, Lee SH, Sarker A, Kim HY, Shin BG, Kim JE (2021) Uptake and carry-over of procymidone residues to non-target succeeding crop from applied on preceding crop. Korean Journal of Environmental Agriculture, 40(3), 203-210. https://doi.org/10.5338/kjea.2021.40.3.24.

29. Xu J, Long X, Ge S, Li M, Chen L, Hu D, Zhang Y (2019) Deposition amount and dissipation kinetics of difenoconazole and propiconazole applied on banana with two commercial spray adjuvants. RSC Advances, 9(34), 19780-19790. https://doi.org/10.1039/c9ra02874a.

30. Heo YJ, Kwak SY, Sarker A, Lee SH, Choi JW, Oh JE, Abdulkareem L, Kim JE (2023) Uptake and translocation of fungicide picarbutrazox in greenhouse cabbage: The significance of translocation factors and home processing. Environmental Science and Pollution Research, 30(14), 40919-40930. https://doi.org/10.1007/s11356-022-25087-x.

31. Hwang KW, Bang WS, Jo HW, Moon JK (2015) Dissipation and removal of the etofenprox residue during processing in spring onion. Journal of Agricultural and Food Chemistry, 63(30), 6675-6680. https://doi.org/10.1021/acs.jafc.5b02345.

32. Sarker A, Nandi R, Kim JE, Islam T (2021) Remediation of chemical pesticides from contaminated sites through potential microorganisms and their functional enzymes: Prospects and challenges. Environmental Technology & Innovation, 23, 101777. https://doi.org/10.1016/J.ETI.2021.101777.

33. Alcântara DB, Fernandes TSM, Nascimento HO, Lopes AF, Menezes MGG, Lima ACA, Carvalho TV, Grinberg P, Milhome MAL, Oliveira AHB, Becker H, Zocolo GJ, Nascimento RF (2019) Diagnostic detection systems and QuEChERS methods for multiclass pesticide analyses in different types of fruits: An overview from the last decade. Food Chemistry, 298, 124958. https://doi.org/10.1016/j.foodchem.2019.124958.

34. Chen B, Shen X, Li Z, Wang J, Li X, Xu Z, Shen Y, Lei Y, Huang X, Wang X, Lei H (2022) Antibody generation and rapid immunochromatography using

time-resolved fluorescence microspheres for propi-conazole: Fungicide abused as growth regulator in vegetable. Foods, 11(3), 324.
https://doi.org/10.3390/foods11030324.

35. Liu S, Huang X, He H, Jin Q, Zhu G (2016) Evaluation of selected plant growth regulators and fungicide residues in fruits for dietary risk assessment. Human and Ecological Risk Assessment: An International Journal, 22(6), 1386-1395.
https://doi.org/10.1080/10807039.2016.1185357.