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Persistence Study of Thiamethoxam and Its Metabolite in Kiwifruit for Establishment of Import Tolerance

Il Kyu Cho^{1,2,3*}, Gyeong Hwan Lee¹, Woo Young Cho^{1,2,5}, Yun-Su Jeong³, Danbi Kim⁴,
Kil Yong Kim⁵, Gi-Woo Hyoung², Chul Hong Kim¹

¹Hyunngong Co. Ltd, Gwangju 61186, Korea, ²Dong Yang Chemical Co., Ltd, D.Y. Environment-Technology. R/Institute, Gwangju 17168, Korea, ³Eco-Friendly Agri-Bio Research Center, Jeonnam Bioindustry Foundation, Gokseong 57510, Korea, ⁴Department of Agro-Food Safety and Crop Protection, National Institute of Agricultural Sciences, Wanju 55365, Korea, ⁵Department of Agriculture and Biological Chemistry, Chonnam National University, Gwangju 61186, Korea

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ORCID

Il Kyu Cho

<https://orcid.org/0000-0002-4177-5588>

Woo Young Cho

<https://orcid.org/0000-0003-2802-6205>

Yun-Su Jeong

<https://orcid.org/0000-0003-2029-6307>

Danbi Kim

<https://orcid.org/0000-0002-8819-3235>

Kil Yong Kim

<https://orcid.org/0000-0002-1752-2908>

Gi-Woo Hyoung

<https://orcid.org/0000-0002-2961-3885>

Chul Hong Kim

<https://orcid.org/0000-0001-5719-6022>

Abstract

BACKGROUND: Pre-harvest interval and decline pattern of thiamethoxam were determined in kiwifruit using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The study was carried out to propose import tolerance using OECD maximum residue limit (MRL) calculator for the export promotion of kiwifruit to Taiwan. **METHODS AND RESULTS:** The thiamethoxam residue in kiwifruit was determined by using the LC-TriQ-MS/MS with the analytical process to set up the import tolerance under greenhouse conditions for Taiwan. Excellent linearity was observed for all of the analytes with a determination coefficient (R^2) ≥ 0.99 . The limit of quantification was determined to be 0.01 mg/kg for both thiamethoxam and clothianidin in kiwifruit.

Linearity was determined from the co-efficient of determinants (R^2) obtained from the seven-point calibration curve. The standard calibration curve showed as follows; 1) Site 1 (Gimje): $y = 944,406X + 1,583$ ($R^2=0.9995$), 2) Site 2 (Goheung): $y = 1,356,205X + 934$ ($R^2=0.9983$), and 3) Site 3 (Jangheung): $y = 1,239,937X - 3,090$ ($R^2=0.9908$). The residue of thiamethoxam in the kiwifruit for three decline trials showed the range of 0.35 to 0.56 mg/kg in site 1 (Gimje), 0.24 to 0.55 mg/kg in site 2 (Goheung), and 0.28 to 0.42 mg/kg in site 3 (Jangheung), respectively. However, clothianidin was not detected in all of the treatments. The maximum residual amounts (decline) in the samples, sprayed according to the safe-use standard for thiamethoxam 10% WG in kiwifruit (30 days before harvest, 3 sprays every 7 days) were 0.56 mg/kg in site 1, 0.55 mg/kg in site 2, and 0.42 mg/kg in site 3, respectively.

CONCLUSION(S): The import tolerance (IT) of thiamethoxam and clothianidin in kiwifruit.

* Corresponding author: Il Kyu Cho
Phone: +82-62-511-7001; Fax: +82-62-511-3061;
E-mail: ilkyucho@naver.com

thoxam for kiwifruit may be proposed to be 0.9 mg/kg by using the OECD MRL calculator.

Key words: Clothianidin, Import tolerance, LC-MS/MS, OECD maximum residue limit (MRL) calculator, Thiamethoxam

Introduction

The World Health Organization (WHO) has reported that the potential risk of heart diseases, diabetes and cancer could be minimized by consuming 400 grams of fruits and vegetables each day, since they are the natural sources of numerous health benefits. (<https://www.medicalnewstoday.com/articles/271285>) Kiwifruits (*Actinidia chinensis*) are rich in vitamin C content and normally consumed in fresh or as a meal, in plates of blended greens, pies, pudding, and cake filling as well as quinic acid and ascorbic acid are fulfilled by adding this fruit and fruit product in fiery daily diets [1]. This fruit holds the proteolytic stimulus “actinidin” which is basically a zymogen and stable on a broad range of pH. Kiwifruit tissue is abundant in folic acid, potassium, chromium, and vitamin E [1]. However, kiwifruit could be affected by various insect pests such as white peach scale (*Pseudaulacaspis pentagona*) during production. The white peach scale is a common pest in orchards. *P. pentagona* is an extremely invasive and can feed on 221 genera of host plants distributed among 85 plant families in more than 112 countries [2]. The residues of pesticides (chlorpyrifos, thiamethoxam, imidacloprid, imazalil, and fenoxycarb) were found in the fruits and vegetable such as bananas, cabbage, oranges, lemons, grape, potatoes, peaches, peppers, strawberries, tomatoes, mandarins, beet, cabbages [3]. The excess is 5-10 times more minimum permissible level (MPL) for thiamethoxam was found in vegetables contaminated by pesticides [3]. Thiamethoxam, {3-[(2-Chloro-1,3-thiazol-5-yl)methyl]-5-methyl-1,3,5-oxadiazin-4-ylidene} nitroamide, is a systemic insecticide of the neonicotinoid and is used to control of a variety of sucking and chewing insects, primarily aphids, whiteflies and white peach scale. The molecular structure of thiamethoxam is shown in Fig. 1. About 35,000 tons of imported kiwifruit enter Korea each year. On the other hand, average domestic kiwifruit production is about 15,000 tons per year. Moreover, Korean kiwifruit export have

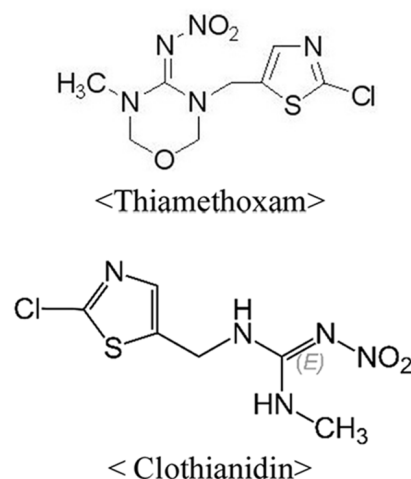


Fig. 1. Molecular structure of thiamethoxam ($C_8H_{10}ClN_5O_3S$, MW.291.71) and clothianidin ($C_6H_8ClN_5O_2S$, MW.249.67).

been increasing recent years. However, export may hindered due to the concern of pesticide residue that may use for crop protection. Therefore, some international organizations like CODEX Alimentarius and European Union imposes pesticide residue limits for each of the pesticides in a specific commodities (Codex Alimentarius, 2019; EU pesticide database). In addition to that some countries such as United States, Japan, Korea, also established their own MRL. International trade of agricultural commodities could be interrupted by the pesticide regulation [4].

A proper balance between the free trade and regulation, public health and crop protection has been an important issue among the international community [4]. Therefore, to meet the needs of international trade, an import tolerance (IT) referred as MRL (Maximum Residue Level) is established for imported agricultural products. In this way, in order to export agricultural products, an exporting country must follow the MRL of importing country. Application of “import tolerance” is required to establish MRL of imported products to facilitate free international trade. A general disharmony of MRLs among the countries has been observed, causes problems for the international trade of agricultural products containing pesticide residues. Therefore, importer or crop producer or pesticide manufacturer can apply for an import tolerance of those active substances that are registered in the importing country or even those which are not.

The Organization for Economic Cooperation and Development (OECD) has developed an MRL calculator that required various field trial residual data in-

cluding decline and harvest test. Since, thiamethoxam is frequently detected in kiwifruit, therefore, prior to export, it is needed to establish IT MRL of thiamethoxam according to the requirement of importing country. Accurate analysis of field supervised sample is necessary for IT MRL that might be an outcome of a robust method. Thiamethoxam has been detected in various matrices using different analytical methodology [5-8]. Among them LC is the most commonly used instrument coupled with traditional or mass spectrometry detector. All of the methodologies use a purification step before injecting to the instrument that makes these method bit lengthy and time consuming. A quick, easy, cheap, effective, and rugged (QuEChERS) method is the most popular extraction method for thiamethoxam in various matrices. However, QuEChERS also involved a d-SPE (dispersive solid phase extraction) purification step using primary secondary amine (PSA) and/or octadecyl C18 sorbent during sample preparation of thiamethoxam.

Utilizing the sensitivity of mass selective detector, QuEChERS method could be modify using dilution as purification instead of d-SPE step. This study aims to find the residues of thiamethoxam 10% WG after foliage spraying on kiwifruit and to establish a Taiwan MRL for thiamethoxam in kiwifruit that have been registered in Korean through setting the Import Tolerance (IT) with OECD MRL calculator.

Materials and Methods

Reagents and Materials

Each 1,000 mg/L of thiamethoxam and clothianidin were obtained from AccuStandard, USA. Thiamethoxam 10% WG (Water dispersible granule) (brand name; Atara) was purchased from Syngenta Korea Co. Ltd. All the reagents used in this study were either organic-residue analytical grade or HPLC grades or analytical grade as confirmed compatibility for residue analysis. Analytical grade formic acid (purity 98%) was commercially available from Junsei Chemical Co., Ltd. (Tokyo, Japan). QuEChERS EN kit containing 4.0 g magnesium sulfate (MgSO_4), 1.0 g sodium chloride (NaCl), 1.0 g trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), and 0.5 g disodium hydrogen citrate sesquihydrate ($\text{C}_6\text{H}_8\text{Na}_2\text{O}_8$) was supplied by Korea Research Institute of Analytical Technology, KRIAT (Daejeon, Republic of Korea).

Preparation of standard solution and calibration

Intermediate standard solution was prepared by diluting stock solution (1000 mg/L) to 100 mg/L using acetonitrile. Working standard solution was prepared by diluting the intermediate standard to 50 mg/L, 10 mg/L, and 5 mg/L using same solvent, which were also used for fortification. Calibration standard was prepared by serial dilution of working standard solution 10 mg/L to 1.0, 0.5, 0.25, 0.1, 0.05, 0.01 mg/L. Matrix matched calibration was prepared by ten times dilution of calibration standard with blank extract and acetonitrile. Both stock solution and intermediate standard were kept in a freezer at -20°C and the working standard solution and calibration standard were placed in a refrigerator at 4°C .

Field experimental design

Three field trials for thiamethoxam and clothianidin in kiwifruit were conducted in three different locations, such as Gimje (site 1), Goheung (site 2) and Jangheung (site 3) in Republic of Korea.

Gimje: The experimental area consists of six individual plots with 50 meter length and 1 meter width for each plot. Among the six plots four was employed for pre-harvest treatment, one was reserved for degradation treatment and one was left as untreated blank. Pre-harvest and degradation plots were equally divided into five parts for replication analysis with 10 meter length for each replicate. In three field trials, the first, and second, plots were treated twice and thrice at 14-7 days and 14-7-2 days respectively prior to harvest. In decline trial kiwifruits were collected from each replicated plot at 1, 3, 7, 14, 21, 28, 35 and 45 days after the commercial thiamethoxam application of three time-treatment at interval of seven days. Goheung: In this site, three plots were employed for commercial pesticide treatment and one plot was remain untouched for control. Among the three plots, two plots were 101 meter length and 1 meter width and another one was 50 meter length and 1 meter width. Each of the two long plots (101 meter) were equally divided by one meter buffer zone and each part was further divided into five replicate for pre-harvest treatment. The third plot with 50 m length and 1 meter width was divided in five parts for replicate analysis and were treated for decline trial. After application, strawberries were collected from each replicated plot at 1, 3, 7, 14, 21, 28, 35 and 45 days. Jangheung: The experimental area comprised of four

plots with 50 m length and 1 m width in which a random block scheme was established with five replicates. In addition, another separated plot (50 m length and 1 m width) was kept untreated for control. The first, and second, plots were treated twice and thrice at 14-7 days and 21-14 days, 14-7-2 days and 21-4-7days respectively prior to harvest.

Sample preparation

A 10 g blank kiwifruit sample was weighing in a 50 mL Teflon centrifuge tube and spiked with a 100 μ L fortification solution. The tube was then kept for one hour for equilibration. A 20 mL of acetonitrile was added to the sample and extract with a geno grinder 2010 (SpexSamplePrep, Metuchen, New Jersey, USA) at 1500 rpm for 1.0 min. QuEChERS EN kit was added to the sample and extract one more time at the same rpm for 1.0 min. The sample was then centrifuged for 5 min at 3500 rpm with a Combi-514R (Hanil Scientific Inc., Gimpo, Republic of Korea). The extract was then five times diluted with acetonitrile and filtered through a syringe filter (0.22 μ m, Futecs Co., Ltd., Korea) before inject to UPLC-MS/MS.

Instrumental conditions

A Waters AQUITY UPLC H Class (Waters, Hertfordshire, UK) coupled with a MS/MS detector (AB SCIEX QTRAP 3500, SCIEX, Redwood, CA, USA) was employed to analyze thiamethoxam at positive electron spray ionization mode. The multi-reaction monitoring (MRM) method for thiamethoxam was initially developed by directly infusing standard (0.1 ppm) using a syringe pump to the MS/MS at 10 μ L/min and tuned automatically according to the mass of the compound. The developed mass transition and optimized parameter are shown in Table 1.

A Shiseido CAPCELL CORE C18 column (2.1 mm \times 100 mm, 2.7 μ m, Shiseido, Tokyo, Japan) was used for analyte separation. A binary mobile phase consisting of 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B) was flowed in an isocratic mode with 45% A. The injection volume was maintained 2 μ L for each of the injection with the column flow of

250 μ L/min.

Method validation

Method was validated following SANTE guideline including parameters: limits of detection (LOD), limits of quantifications (LOQ), linearity, specificity, selectivity, accuracy and precision. A limit of detection is the lowest detectable amount which is three times higher than the baseline noise. Limit of quantification is the lowest concentration that could be recovered following the developed methodology with acceptable precision. Linearity is observed from the coefficient of determinants (R^2) after plotting six point concentrations against area. Specificity is the absence or below 30% interference of LOQ in the blank kiwifruit at the retention time of thiamethoxam. Selectivity is the identical retention time of standard, matrix matched standard and fortified standard. Accuracy is determined from the recovery after fortification of three different concentrations at LOQ, 10xLOQ and 50xLOQ with five replicate for each concentration. Precision is calculated from the relative standard deviation (RSD) of five replicated recovery analysis.

Matrix effect

After comparing the slopes of matrix matched calibration curve and solvent based calibration curve, the overall matrix effect was calculated. Matrix induced response enhancement is occurred with a higher slope. On the other hand, lower slope indicates signal suppression. The matrix effect (ME%) was calculated from the following equation.

$$ME\% = \frac{\text{Slope of matrix matched calibration} - \text{slope of solvent calibration}}{\text{Slope of solvent standard calibration}}$$

Results and Discussion

Establishment of analytical method for thiamethoxam and clothianidin in kiwifruit

Several previous studies have shown that all of the three versions (Original, AOAC, and EN) of QuEChERS

Table 1. Optimized mass transition parameters of thiamethoxam and clothianidin

Compounds	Precursor ion (m/z)	Quantitation ion (m/z)	Confirmation	RT time (min)
Thiamethoxam	291.85	132.00	181.00	1.1~1.2
Clothianidin	249.85	168.95	132.05	1.2~1.4

(Quick, Easy, Cheap, Effective, Rugged, and Safe) method were effective for extraction and purification of thiamethoxam in various matrices [8-15]. Among them best recovery was found to achieved through QuEChERS EN method. In general, QuEChERS method consists of extraction with acetonitrile and salts and purification was performed via dispersive solid phase extraction procedure (d-SPE) with primary secondary amine (PSA), Octadecyl C18, and/or GCB. However, due to the sensitivity of UPLC-MS/MS which helps to attain low limit of quantification, could be utilized for dilution as purification instead of time consuming d-SPE purification. Therefore, in the present study, sample extraction was carried out via QuEChERS EN method and dilution was performed for purification [16].

Method validation

The thiamethoxam residue in kiwifruit was determined by using the LC-TriQ-MS/MS with analytical process to set up the Import tolerance under greenhouse conditions in Taiwan. Linearity was determined from the co-efficient of determinants (R^2) obtained from the seven-points calibration curve. The standard calibration curve showed as follows; 1) Site 1 (Gimje): $y = 944,406X + 1,583$ ($R^2=0.9995$), 2) Site 2 (Goheung): $y = 1,356,205X + 934$ ($R^2=0.9983$), 3) Site 3 (Jangheung): $y = 1,239,937X - 3,090$ ($R^2=0.9908$). Matrix effect was compensated by constructing matrix matched calibration and the effect was calculated by comparing the slope of the matrix matched calibration and the slope of the matrix free solvent calibration Table 2. Method validation was carried out via single laboratory analytical approach following the method [16]. Recovery and repeatability at LOQ level for thiamethoxam and clothianidin were found as 75.0-100.7% and 75.4-99.9%, respectively. The LOQ at 0.01 mg/kg level was recovered at acceptable range of accuracy (70-120%) and

precision (<20%). LOQ at 0.01 mg/kg is low enough to quantify thiamethoxam and clothianidin for calculation of import tolerance as the maximum residue limit of thiamethoxam and clothianidin are 0.5 mg/kg and 1.0 mg/kg, respectively, in three application at 30 days before harvest for kiwifruit after a preharvest interval (PHI) of 7 days, while the European Union (EU) maximum residue level (0.3 mg/kg for thiamethoxam; 0.2 mg/kg for clothianidin) in cowpea after a preharvest interval (PHI) of 7 days. Thiamethoxam 10% WG were sprayed according to the safe-use guidelines, three application at 30 days before harvest for kiwifruit as the formulation of thiamethoxam product. The average recovery of thiamethoxam and clothianidin in kiwifruit showed 82.7 ± 2.4 - 100.7 ± 11.3 , 73.6 ± 6.3 - 84.5 ± 5.0 and 75.0 ± 2.7 - $91.3 \pm 9.0\%$ respectively in the three sites Table 3. Furthermore, this level of LOQ is supported by "positive list system (PLS)", used for enhancing international trade.

Linearity and matrix effect

A six point matrix matched calibration curve was prepared including concentration 0.01, 0.05, 0.1, 0.25, 0.5, 1.0 mg/kg. Excellent linearity was observed from the curve with determinant coefficient, $R^2 \geq 0.9998$. Matrix suppression effect was observed for thiamethoxam in kiwifruit s for all of the sites and shown in Table 2.

Specificity and selectivity

Fig. 2 shows the chromatograms of standard (A), blank (B), and recovery (C). At the retention time of standard thiamethoxam, blank chromatograms (B) contains no interferences indicated that the method is specific. The identical retention time of standard thiamethoxam peak (Chromatogram A) and the recovery peak (Chromatogram C) confirm about the selectivity of the method.

Table 2. Regression parameters for thiamethoxam and clothianidin calibration curve

Location	Analyte	Matrix	Regression equation	R^2	Calibration range ($\mu\text{g/L}$)	Matrix effect (%)
Site 1 (Gimje)	Thiamethoxam	kiwifruit	$Y = 944401X + 1583$	0.9995	10-200	0.58
	Clothianidin		$Y = 1664094X + 139$	0.9997	10-200	0.34
Site 2 (Goheung)	Thiamethoxam	kiwifruit	$Y = 1356205X + 935$	0.9983	10-200	0.53
	Clothianidin		$Y = 1959747X + 997$	0.9977	10-200	0.46
Site 3 (Jangheung)	Thiamethoxam	kiwifruit	$Y = 1239937X - 3091$	0.9987	10-200	0.59
	Clothianidin		$Y = 1719046X - 2913$	0.9989	10-200	1.01

Table 3. LOQ, linearity and recovery of thiamethoxam and clothianidin in kiwifruit at three different sites

Compound	Location	Linearity (R ²)	LOQ (mg/kg)	Recovery±RSD ^a (%)		
				LOQ	10 LOQ	100 LOQ
Thiamethoxam	Site 1 (Gimje)	0.9995	0.01	100.7±11.3	91.8±5.0	84.6±6.1
	Site 2 (Goheung)	0.9983		73.6±6.3	77.8±5.9	77.8±6.3
	Site 3 (Jangheung)	0.9987		91.3±9.0	75.2±4.3	75.0±2.7
Clothianidin	Site 1 (Gimje)	0.9997	0.01	99.9±4.1	83.3±2.9	82.7±2.4
	Site 2 (Goheung)	0.9977		81.7±1.3	73.3±4.2	84.5±5.0
	Site 3 (Jangheung)	0.9989		83.2±4.8	77.3±2.7	75.4±3.2

^a Mean values of 5 times repetitions with relative standard deviation (RSD)

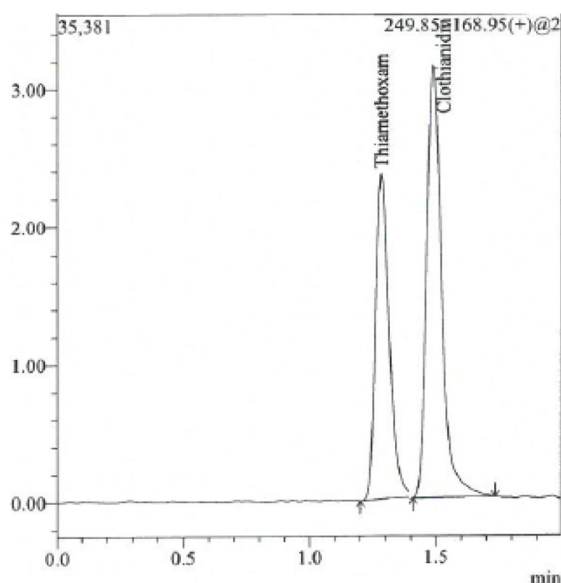


Fig. 2. UPLC-MS/MS chromatograms of separation for thiamethoxam and clothianidin-matrix matched standard 0.1 mg/kg.

Accuracy and precision

Accuracy was determined from recovery of standard thiamethoxam at three different concentrations (LOQ, 10LOQ and 50LOQ) spiking to the blank kiwifruit sample with five replicate for each concentration. Thiamethoxam 10% WG were sprayed according to the safe-use guidelines of it for kiwifruit as the formulation of thiamethoxam product. The average recovery of thiamethoxam and clothianidin in kiwifruit showed 73.6±4.6-100.7±11.4 and 75.4±3.2-99.9±4.1% respectively in the three sites Table 2. The precision of the developed method was reflected from the repeatability (RSD) of the five times replicated analysis which was found 2.23-6.50% for site 1, 1.14-3.09% for site 2 and 0.80-3.61% for site 3. Both recovery and RSD were in acceptable range according to the SANTE guideline (70-120%, and <20%) (SANTE, 2017).

UPLC-MS/MS analysis

A 0.1 ppm standard thiamethoxam and clothianidin in solvent were directly infused to the MS/MS with the infused rate of 10 µL/min for optimizing ionization mode, precursor ion, product ions, collision energy, and cone voltage. The compounds were tuned automatically with the molecular weight of 291.85 and 249.85, respectively, for optimizing analyte ionization. The sensitivity of the target compound was examined in both positive and negative electrospray ionization (ESI) mode. At full scan range, the strong response of thiamethoxam and clothianidin were observed when the MS/MS were operated at positive mode. For detection and quantification of compound two mass transitions were chosen at multiple reaction monitoring (MRM) mode. The transition with the maximum intensity of thiamethoxam (291.85→132.00) was used as quantitative ion and comparatively less intense transition (291.85→181.00) was used for quality confirmation. The compound was retained at 1.66 minute within a short run time window (5 min) at isocratic mode Table 1.

Field treated residues

The validated method was applied to the field treated kiwifruit sample for analyzing harvest and decline residues of thiamethoxam at three different fields with the variability of temperature and humidity. The storage stability of thiamethoxam and clothianidin in kiwifruit were shown in the Table 4. The decline residue data of thiamethoxam was shown in the Table 5, while clothianidin, a metabolite of thiamethoxam did not detected in the all samples. In the case of decline trial Table 5, the highest residues were 0.53 mg/kg, 0.50 mg/kg and 0.37 mg/kg, respectively in site 1, 2 and 3 at 0 day. The residue was continuously and gradually decayed with days after application (0, 7, 14, 21, 30, 40 days) and at 40 days the residue was found

Table 4. Storage stability of thiamethoxam and clothianidin in kiwifruit

Field	Compounds	Fortification level (mg/kg)	Storage period (days)	Recovery \pm RSD ^a (%)
Site 1 (Gimje)	Thiamethoxam	0.1	109	97.3 \pm 5.1
	Clothianidin		109	85.5 \pm 3.0
Site 2 (Goheung)	Thiamethoxam		103	70.3 \pm 3.1
	Clothianidin		103	73.1 \pm 1.0
Site 3 (Jangheung)	Thiamethoxam		116	71.5 \pm 1.8
	Clothianidin		116	72.8 \pm 1.1

^a Mean values of 3 times repetitions with relative standard deviation (RSD)

Table 5. Decline residues of thiamethoxam in kiwifruit at three different sites

DALA ^a	Residues ^b \pm SD (mg/kg)			Application
	Site 1 (Gimje)	Site 2 (Goheung)	Site 3 (Jangheung)	
0	0.53 \pm 0.02	0.50 \pm 0.04	0.37 \pm 0.04	Three times at interval of 7 days (14-7-0)
7	0.38 \pm 0.01	0.41 \pm 0.04	0.31 \pm 0.01	
14	0.40 \pm 0.07	0.35 \pm 0.06	0.31 \pm 0.05	
21	0.38 \pm 0.03	0.21 \pm 0.04	0.26 \pm 0.03	
30	0.33 \pm 0.03	0.25 \pm 0.06	0.29 \pm 0.02	
40	0.33 \pm 0.06	0.27 \pm 0.04	0.28 \pm 0.03	

^a Days after last application, ^b Mean values of three repetitions

0.27-0.33 mg/kg in the three of sites. The residue of thiamethoxam in the kiwifruit for three decline trials showed in the range of 0.33 to 0.53 mg/kg in site 1 (Gimje), 0.25 to 0.50 mg/kg in site 2 (Goheung) and 0.28 to 0.37 mg/kg in site 3 (Jangheung), respectively. However, the clothianidin did not detected in all of treatment. The maximum residual amount (decline) in the sample sprayed according to the safe-use standard for thiamethoxam 10% WG in kiwifruit (30 days before harvest, 3 sprays every 7 days) is 0.33 mg/kg in site 1 and 0.25 mg/kg in site 2 and 0.29 mg/kg in site 3, respectively Table 5 and Fig. 3.

Dissipation of thiamethoxam and its metabolite clothianidin in kiwifruit

The original deposition values of thiamethoxam in kiwifruit are 0.21 and 0.53 mg/kg for the site 1, site 2 and site 3, respectively Table 5. As shown in the Table 6, the dissipation equation of the Gimje site was $Y=4.773e^{-0.0114}$ ($R^2=0.8953$) with half-life of 61 days, and for the Goheung site, $Y=4.475e^{-0.0206}$ ($R^2=0.8256$) with half-life of 34 days, and for the Jangheung site, $Y=3.50e^{-0.0066}$ ($R^2=0.7464$) with half-life of 106 days. Thiamethoxam degraded more slowly in kiwifruit from Jangheung site.

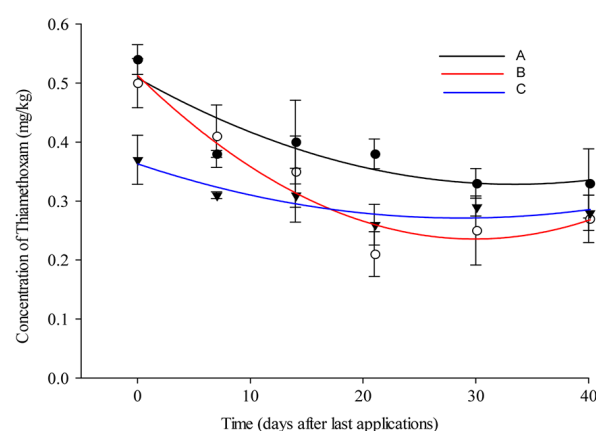


Fig. 3. Residual change of thiamethoxam in kiwifruit three different sites (A; Gimje, B; Goheung, C; Jangheung).

Whereas in Goheung, 50% residue dissipation occurred within the 40 days. This result was different with the study [16] that thiamethoxam degraded more quickly in cowpea, with 1 day, approximately 48% of thiamethoxam residue dissipated from cowpea in Beijing, whereas in Anhui, 54% residue dissipation occurred within the same period. In the exponential decay study for dissipation of thiamethoxam and clothianidin in crop [16-19], it was reported that persistence of the thiamethoxam and clothianidin in crop could be

Table 6. Exponential decay fit of the data for the dissipation rates of and thiamethoxam in kiwifruit

Field sites	Exponential decay equation	R ²	DT ₅₀ (days)
Gimje	$Y = 4.722e^{-0.0114}$	0.8953	61
Goheung	$Y = 4.475e^{-0.0206}$	0.8256	34
Jangheung	$Y = 3.350e^{-0.0066}$	0.7464	106

affected by physicochemical properties of soil such as pH, organic matter, clay content, growth temperature, rain, humidity and light intensity may have also played a significant in thiamethoxam residue.

OECD maximum residue limit

The decline residual data of thiamethoxam in kiwifruit were inserted to the OECD maximum residue limit calculator which provided rounded maximum residue limit of 0.9 mg/kg, considering the residue of thiamethoxam of 0.18-0.310 mg/kg at the safe-use standard of 30 days before harvest of three-time appli-

cation for various decline trial Table 7. Therefore, the rounded MRL 0.9 mg/kg extracted from OECD maximum residue limit calculator was considered as import tolerance or maximum residue limit for thiamethoxam in kiwifruit. The MRL determined here is higher than as the MRL (0.5 mg/kg) established by the Ministry of Food and Drug Administration, Republic of Korea (Pesticide MRLs in Food, 2017).

Conclusion

A MRL of each OECD nation in the world has been set for the quarantine of residual pesticides among domestic agricultural products. The import tolerance (IT) is needed for international trade and the IT is able to be derived from OECD MRL calculator with several residual field trials. IT can be either similar with the country domestic MRL or different from it. Therefore, IT must be calculated by the request of importing country for the purpose of international trade. In this study, the IT of thiamethoxam in kiwifruit was established using OECD maximum residue limit calculator. Three supervised field trial study was carried out at different places of Republic of Korea to observe harvest and decline residue at different climatic conditions. A single laboratory validated method with excellent accuracy and precision was applied to the field sample for residue determination using UPLC-MS/MS. The extracted MRL from OECD maximum residue calculator was found 0.9 mg/kg, which is exactly the same as the MRL established by Ministry of Food and Drug Administration, Republic of Korea.

Note

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Table 7. Calculation of maximum residue limit for thiamethoxam in kiwifruit via OECD calculator for maximum residue limit

Compound	Thiamethoxam	
Crop	Kiwifruit	
Region / Country	Korea	
GAP	30 DALA (3 times application)	
Total number of data (n)	9	
Percentage of censored data	0%	
Number of non-censored data	9	
Lowest residue	0.180	
Highest residue	0.350	
Median residue	0.290	
Mean	0.289	
Standard deviation (SD)	0.048	
Correction factor for censoring (CF)	1.000	
Proposed MRL estimate		
- Highest residue	0.350	
- Mean + 4 SD	0.480	
- CF x 3 Mean	0.867	
Unrounded MRL	0.867	
Rounded MRL	0.9	
Residues (mg/kg)		
Site 1 (Gimje)	Site 2 (Goheung)	Site 3 (Jangheung)
0.300	0.290	0.310
0.350	0.180	0.280
0.330	0.270	0.290

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