Biological Forum – An International Journal **15(10): 675-678(2023)**

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Dissipation Kinetics and Risk Assessment of Thiamethoxam 25% WG in Chilli, *Capsicum annuum* L.

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(Received: 05 August 2023; Revised: 27 August 2023; Accepted: 25 September 2023; Published: 15 October 2023)
(Published by Research Trend)

ABSTRACT: Dissipation and risk assessment of 25 % thiamethoxam WG in chillies were carried out at the Pesticide Residue Research and Analytical Laboratory, College of Agriculture, Thiruvananthapuram. Since chilli is an important spice crop, it is routinely used in every Indian kitchen on an everyday basis, both directly and indirectly. So, it is very important to identify the amount of contaminants adhered to the product and its safety before consumption. Insecticide residue analysis of thiamethoxam was done, and a residue of 0.17 mg kg^{-1} was observed on the chilli after two hours of spraying. The residue reached below the limit of quantification on the fifth day after spraying. The risk assessment showed that the theoretical maximum residue contribution (TMRC) value was lower than the maximum permissible intake (MPI) value from the day of spraying, making the product safe for consumption.

Keywords: Thiamethoxam, Chilli, Risk assessment, Insecticide residue, Dissipation, TMRC, MPI, LOQ, LC-MS/MS.

INTRODUCTION

Chilli is a major spice and vegetable crop that is widely grown throughout the world. In India, 309 thousand hectares of chilli were planted, yielding 3592 thousand tons of output. In terms of international trade, India maintains its top spot, with approximately 30% of its entire production exported, accounting for 37% of global production. Although India is the world's largest producer of chillies, its productivity is only 11.62 T ha^{-1} (Raju *et al.*, 2023). The sucking pests that affect chilli at various crop stages, including mites, *Polyphagotarsonemus latus*, thrips, *Scirtothrips dorsalis*, aphids, *Myzus persicae*, and *Aphis gossypii*, are an especially prominent limitation to productivity. Applying insecticides is seldom one of the farmer's methods for reducing pest infestations, yet this practice leads to significant chemical residue buildup on crops and the environment. Thiamethoxam, a neonicotinoid insecticide, has been extensively used against various sucking pests of chilli (Sujay *et al.*, 2015). Hence, the present study was carried out to identify the kinetics and dissipation pattern of thiamethoxam on chilli.

MATERIALS AND METHODS

A field experiment was conducted at Kalliyoor Panchayath in Thiruvanathapuram district, Kerala, to determine the dissipation behavior of thiamethoxam 25% WG on chilli. A randomized block design with five replications was employed as the statistical design. The crop (Variety: Vellayani Athulya) was grown in accordance with the Kerala Agricultural University's Package of Practices. Thiamethoxam 25% WG (Actara) @ 50 g a.i. ha^{-1} was given using a hand-operated knapsack sprayer while in the fruiting period. The spray volume was 500 L ha^{-1}. Fresh chilli fruits (250 g) were randomly gathered from each replica after 0 (after 2 h), three, five, seven, ten, fifteen, and thirty days after the application of insecticide. Each replicate's samples were collected and brought to the Pesticide Residue Research and Analytical Laboratory (PRRAL), College of Agriculture, Vellayani, Thiruvanathapuam, for residue analysis.

For the extraction and clean-up of residues in chilli, the multiresidue estimation process outlined for vegetables by QuEChERS has been employed with sufficient modifications. The fruits were mashed in a high-speed blender (BLIXER 6 vv Robot Coupe), and an adequate sample of 25 g of chilli was taken in a 250 mL centrifuge bottle. HPLC-grade acetonitrile (50 mL) was added to the samples and homogenized for a period of three minutes using a high-speed tissue homogenizer (Heidolph Silent Crusher-M) at 1400 rpm. Following that, ten grams of activated sodium chloride (NaCl) were added and vortexed for two minutes in order to separate the acetonitrile layer. Following centrifuging the samples for eight minutes at 2500 rpm, sixteen milliliters of the clear top layer were moved into a fifty-milliliter centrifuge tube holding six grams of activated sodium sulfate and agitated for a total of two minutes.

Dispersive solid-phase extraction (DSPE) was employed to clear up the acetonitrile extracts. Twelve milliliters of the topmost layer were added into centrifuge tubes holding 0.20 g PSA (primary secondary amine) and 1.2 g magnesium sulfate for this purpose. The tubes went through a centrifuge for a duration of five minutes at 2500 rpm. The liquid that remained from the supernatant has been put into a turbovap tube and dehydrated to dryness at 40°C and 7.5 psi nitrogen flow. The residues were reconstituted in 1.5 mL of methanol, filtered through a 0.2 micron filter (PVDF) and estimated in LC- MS/MS.

Recovery studies have been carried out to measure the success of the extraction and the cleanup methods that were employed to standardize the method for quantifying the residual insecticides from chilli. The control samples of chilli were independently spiked at various concentrations with the certified reference material (CRM) of thiamethoxam for the purpose of the study. CRM of thiamethoxam, having 99.3% purity, has been purchased from M/s Sigma Aldrich for method validation. Standard solutions of the insecticide (1000 g mL^{-1}) were created by mixing a weighed amount of an analytical-grade substance in methanol. The initial solution of the stock was repeatedly diluted to make a 100 g mL^{-1} intermediate stock. The resulting intermediate stocks have been diluted subsequently with methanol to make a working standard of 10 g mL^{-1}. The working standard formulations were serially diluted to reach concentrations of 1.00, 0.50, 0.25, 0.10, 0.05, 0.01, and 0.005 g mL^{-1}.

Chilli (five hundred grams) taken from the control plots were diced and mixed to a fine paste for fortification and recovery trials. Five replicates of twenty-five grams of fruits were added in fifty milliliter centrifuge tubes and contaminated with 0.05 (LOQ), 0.25 (2 times LOQ), and 0.50 (5x LOQ) mL^{-1} (LOQ-limit of quantification) of the working standard of thiamethoxam prepared. The extraction and clean-up were carried out using the QuEChERS method (Anastassiades *et al.,* 2003), and the quantification was carried out using LC-MS/MS under optimal conditions. A method with an insecticide recovery rate of 70 to 120 per cent and a relative standard deviation of less than 20 was deemed ideal.

The quantity of residues has been estimated using the peak region of the chromatogram as a guide, that is, pesticide residue (mg kg^{-1}) = concentration obtained from the chromatogram by using the calibration curve × dilution factor. Apart from the residue concentration in the chilli, its half-life value was also important. So, the residue data acquired at various intervals underwent statistical analysis according to the method established by Hoskins (1961) to calculate the half-lives values for those insecticides on the treated substrates.

Pesticides enter the body via the gastrointestinal tract at a considerably higher rate than through other routes such as air and water intake (Claeys *et al.,* 2011). As a result, it is critical to examine the possible harm of insecticides to human health. Risk assessment is merely a mathematical calculation to make sure that an item is safe for ingestion. The risk assessment's major goal is to identify the safe limits of agricultural chemicals so that their adverse effects on human diets can be managed. The risk was evaluated by comparing the acceptable daily intake (ADI) value with the maximum permissible intake (MPI) of pesticide residues through produce and the theoretical maximum residue contribution (TMRC). For risk assessment studies of insecticides, WHO established an ADI value of 0.08 mg kg^{-1} body weight day^{-1} for thiamethoxam.

RESULT AND DISCUSSION

Method validation experiments gave satisfactory recovery, and hence the method employed for residue analysis was found to be effective (Table 1). The average percentage of recovered thiamethoxam found within the acceptable limits of 84.00, 101.33, and 77.83% at fortification levels of 0.05, 0.25 and 0.50 mg Kg^{-1}, respectively. The repeatability of the recovery data, demonstrated by relative standard deviations (RSD 20 %), revealed that the procedure was sufficiently trustworthy for pesticide residue analysis.

The average residues, dissipation percentage, and half-lives are depicted in Table 2. The residues of thiamethoxam on chilli reached below LOQ on the fifth day after spraying onwards. The initial residue was found to be 0.17 mg Kg^{-1}. The initial residues decayed at a rate of 47.05 % on the first day after spraying, reaching an amount of 0.09 mg Kg^{-1}. On the third day after spraying, an average residual of 0.07 mg Kg^{-1} was discovered with a dissipation percentage of 58.82. It is evident that on the third day after spraying, more than 50 % of the thiamethoxam was dissipated, and residue levels fell below LOQ starting on the fifth day following spraying. The dissipation appears to follow first-order kinetics. The calculated half-life was 4.49 days. More or less similar results were obtained by (Pathipati *et al.*, 2018). They discovered a preliminary accumulation of 1.62 mg kg^{-1} when chilli plants were treated with thiamethoxam at 25 % WG at 50 g a.i. ha^{-1} and the leftovers fell below the limit of detection (0.05) on the seventh day following spraying. According to published research, thiamethoxam dissipates 95.2 % in okra fruits on the fifth day after application at fruiting stages (Singh and Kulshrestha 2005), which is in keeping with our findings on chilli. (Chauhan *et al.*, 2013) also reported a half-life of 1.47 days for thiamethoxam in okra fruits with a similar dissipation trend. Reddy *et al.* (2022) discovered that the vegetable cowpea sprayed with thiamethoxam had an initial residue of 0.5 g g^{-1} that lasted for a period of three days. On the fifth day, the residues were below the quantification level, and this result is obviously in line with the present investigation. The same style of residue dissipation of thiamethoxam (0.016 %) in mango has been found by Bhattacherjee and Dikshit (2016), and its dissipation followed kinetics of first order with a half-life of 4.5 days. Thiamethoxam was shown to dissolve from 82 to 87 % in tomato fruits in 10 days, with a half-life of 4 days (Karmakar and Kulshrestha 2009).

In a healthy diet, a typical Indian takes five grams of fresh chili (NSSO, 2014). The MPI was calculated by multiplying the ADI by the mean weight of an Indian person, which is 60 kg (Katna *et al.*, 2017). If the TMRC values are lower compared to the MPI values, the risk is stated to be zero, and the produce is safe to eat. Table 3 shows the risk evaluation of thiamethoxam on chilli.

Thiamethoxam's ADI is 0.08 mg kg^{-1} bw day^{-1}. The MPI value was calculated to be 4800 g $person^{-1}$ day^{-1}. The insecticide arrived at LOQ 5 days after spraying. TMRC readings were calculated to be 0.85, 0.45, and 0.35 g $person^{-1}$ day^{-1} at zero, one, and three days after spraying, respectively. The calculated TMRC values are far below the MPI values, so the risk associated with spraying thiamethoxam on chilli was deemed zero, and the product was declared safe for human consumption. According to the risk assessment table, the TMRC value from zero to three days following spraying is too far behind the MPI values, and hence it can be deemed a pesticide with no risk to chilli. Furthermore, the chilli remained safe for human consumption on the day of treatment because the residues left on the fruits were much lower than the MPI. According to Bhattacherjee and Dikshit (2016), the TMRC for thiamethoxam was lower than the MPI, implying that it is not eligible as a consumer hazard.

Venkateswarlu *et al.* (2007) demonstrated that the amount of thiamethoxam remaining in grape samples collected from a field in Hyderabad, India, was within the allowable level. As reported by Hem *et al.* (2010), the detected thaimethoxam residues in pomegranate also turned out to be considerably less than its MRL level (0.5 mg kg^{-1}).

Thiamethoxam dissipation followed the kinetics of the first order and reached LOQ on the fifth day after spraying. In terms of TMRC values, it was significantly lower than MPI two hours after spraying. As a result, it was deemed safe for consumption on the day of spraying. To put it another way, an adult weighing 60 kg can safely consume 0.85 g of thiamethoxam without risking his or her life. Because of these features, the specific insecticide can be used safely at the appropriate level against the sucking insect of chilli without posing any health risks to people.

Table 1: Thiamethoxam recovery rate in chilli (%).

Insecticide	Fortification levels (mg Kg^{-1})					
	LOQ*		2 LOQ		5 LOQ	
	Mean recovery (%)	RSD** (%)	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Thiamethoxam	84.00	8.25	101.33	4.56	77.83	12.22

*Limit of quantification (LOQ) – 0.05 mg kg^{-1}, **RSD- Relative standard deviation

Table 2: Residue and dissipation pattern of of thiamethoxam 25% WG in chilli fruits.

DAS*	Thiamethoxam 25% WG @ 50g a.i g ha^{-1}	
	Mean residue± SD*** (mg Kg^{-1})	Dissipation (%)
0(2h after spraying)	0.17 + 0.001	-
1	0.09 + 0.011	47.05
3	0.07 + 0.010	58.82
5	< LOQ**	
7	< LOQ	
10	< LOQ	
15	< LOQ	
30	< LOQ	
Half-life (days)	4.49	

*DAS- Days after Spraying; **LOQ - Limit of quantification (0.05 mg kg^{-1}); ***SD- Standard Deviation

Table 3: Risk assessment of thiamethoxam 25 % WG.

ADI* (mg kg^{-1} bw d^{-1})	Average body weight (kg)	Interval (Days)	Daily Consumption rate (g day^{-1})	MPI** (μg $person^{-1}$ day^{-1})	Average residue (μg g^{-1})	TMRC*** (μg $person^{-1}$ day^{-1})
0.08	60	0	5	4800	0.17	0.85
0.08	60	1	5	4800	0.09	0.45
0.08	60	3	5	4800	0.07	0.35
0.08	60	5	5	4800	<LOQ	-
0.08	60	7	5	4800	<LOQ	-
0.08	60	10	5	4800	<LOQ	-
0.08	60	15	5	4800	<LOQ	-
0.08	60	30	5	4800	<LOQ	-

*ADI – Acceptable Daily Intake, **MPI – Maximum Permissible Intake, **TMRC – Theoretical Maximum Residue Concentration, MPI = ADI × Average body weight × 1000, TMRC = Daily consumption rate × Average residue

CONCLUSIONS

On chillies, the thiamethoxam 25 % WG dissipation pattern adhered to first-order kinetics. After spraying, the thiamethoxam residues on the chilli reached below the limit of quantification on the fifth day. The first residue measured out to be 0.17 mg Kg^{-1}. The initial residues decayed at a rate of 47.05 per cent on the first day following spraying, reaching a total of 0.09 mg Kg^{-1}. Given the TMRC readings, it was significantly lower than the MPI measured two hours after the spraying event. Because of this, it was deemed safe to eat on the day it was sprayed. To be more precise, an adult weighing 60 kg can comfortably withstand a consumption of 0.85 μg of thiamethoxam without experiencing a significant risk to their life. All these factors mean that the specific insecticide can be used safely against the sucking pest of chilies at the appropriate level without endangering human health.

FUTURE SCOPE

These days, it's not uncommon to apply pesticides and other chemicals to agricultural products. There are situations where it might not be able to produce goods without using pesticides. Knowing whether the harvested product has pesticide residues is crucial in these situations. The quantity of residue in the harvested agricultural commodity may be clearly seen using the QuEChERS method of pesticide residue measurement, and harvesting time can then be computed based on this information. These days, risk assessment studies are crucial because, particularly in developed nations, the MRL determines the import and export of food commodities. As a result, the scope and significance of residue analysis and pesticide risk assessment will grow in the future.

Acknowledgements. The authors thank the Kerala Agricultural University and for providing necessary funds.
Conflict of Interest. None.

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How to cite this article: Anju Viswanathan K. and Ambily Paul (2023). Dissipation Kinetics and Risk Assessment of Thiamethoxam 25% WG in Chilli, *Capsicum annuum* L. *Biological Forum – An International Journal, 15*(10): 675-678.