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DISSIPATION KINETICS AND RISK ASSESSMENT OF THIAMETHOXAM 25 % WG RESIDUES IN VEGETABLE COWPEA

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ABSTRACT

A field experiment was conducted to study the rate of dissipation of thiamethoxam 25% WG in vegetable cowpea. Thiamethoxam 25%WG @ 0.24 ml l^{-1} was sprayed at pod formation stage, and samples of pods were harvested at 0 (2 hr after spray), 1, 3, 5, 7, 10, 15 days after spray. Residues were estimated using liquid chromatography tandem mass spectrometer (LC-MS/ MS) at the All-India Network Project on Pesticides Residues, College of Agriculture, Vellayani, Kerala. The mean initial residue was found to be 0.53 µg g^{-1}, and residues were observed persisting up to three days and reached below quantification level on fifth day.

Key words: Dissipation, thiamethoxam, cowpea, food safety, LC-MS/MS, linearity, recovery, risk assessment, limit of detection

Cowpea or the yard long bean (*Vigna unguiculata* subsp. *sesquipedalis* (L.) Verdc.) is a popular vegetable grown in Africa, Latin America, Southeast Asia, and southern USA (Feleke et al., 2006). Though an array of pests attacks this crop, the major loss is incurred from the infestation by pod borers followed by sucking pests viz., aphid and pod bug causing up to 80% yield losses (Sharma, 1998). Thiamethoxam is a second-generation neonicotinoid insecticide. It binds to nicotinic acetyl choline receptors in the central nervous system and is presently one of the most effective pesticides against aphids, whiteflies and thrips. The use of pesticides on any crop or commodity may lead to its residues remaining at the time of harvest. The continuous ingestion of these residues, though in small quantities, can result in their accumulation in the body causing adverse effects on human health. Thus, the knowledge of the nature and amount of chemicals, which remain in food commodities at the time of their consumption, is very important from public health point of view. The assessment of hazards from these small quantities of pesticides in food and environment, therefore, has become an important part of the overall risks/ benefits evaluation before a pesticide is recommended for use (Bates, 1982). Since, literature pertaining to the persistence behaviour of thiamethoxam residues on cowpea is scanty, the present study was undertaken.

MATERIALS AND METHODS

The trial was undertaken in 2017 kharif season at the farmers field, Kalliyoor Vellayani, Thiruvananthapuram to observe the dissipation pattern of thiamethoxam in vegetable cowpea. All the practices were followed as per KAU package of practices in raising the crop. Thiamethoxam 25% WG (Actara) was procured from local market and applied at pod formation stage as foliar spray @ 30 g a.i ha^{-1}. Two sprays were given at 15 days interval. Cowpea (500 g) pods harvested from control plots were chopped and ground to a fine paste. Five replicates of 25 g representative samples were taken in 50 ml centrifuge tubes and spiked with 0.05, 0.25 and 0.50 ml of 10 µg ml^{-1} working standard of the insecticide. The extraction and clean-up were done following the QuEChERS method (Anastassiades et al., 2003) and quantified using LC-MS/MS under optimized conditions. The method which gave recovery of thiamethoxam in the range of 70-120% with a relative standard deviation < 20 was considered to be the ideal method and the lowest spiking level was considered as LOQ. The recoveries were identified as 84.00, 101.33 and 77.83 at 0.05, 0.25 and 0.5 levels, respectively.

Matured cowpea pods (2 kg each) sprayed with thiamethoxam were collected at 2 hr, and one, three, five, seven, ten and fifteen days after spraying and brought to the laboratory and processed immediately. A representative sample of 25g of ground cowpea was taken in a 250 ml centrifuge tube. HPLC grade acetonitrile (50 ml) was added to the samples and homogenized with a high-speed tissue homogenizer (Heidolph Silent Crusher-M) at 14000 rpm for 3 min. This was followed by the addition of 10 g activated sodium chloride (NaCl) and vertexing for 2 min for separation of the acetonitrile layer. The samples were then centrifuged for 5 min at 2500 rpm and 12 ml of the clear upper layer was transferred into 50 ml centrifuge tubes containing 6 g pre-activated sodium sulphate and vortexed for 2 min. The acetonitrile extracts were subjected to clean up by dispersive solid phase extraction (DSPE). For this, 8 ml of the upper layer was transferred into centrifuge tubes (15 ml) containing 0.20 g primary secondary amine and 1.20 g magnesium sulphate. The aliquot was then shaken in vortex for 2 min and again centrifuged for 5 min at 2500 rpm. The supernatant (5 ml) was transferred to turbovap tube and evaporated liquid to dryness under a gentle steam of nitrogen using a turbovap set at 40 ºC and 7.5 psi nitrogen flow. The residue was reconstituted in 2 ml of methanol and filtered through a 0.2-micron filter (PVDF) prior to estimation in LC-MS/MS. Based on the peak area of the chromatogram obtained for insecticide, the quantity of residue was determined as follows- Pesticide residue (mg kg^{-1}) = Concentration obtained from chromatogram by using calibration curve × Dilution factor.

The persistence of insecticides is generally expressed in terms of half-life (DT50) i.e., time for disappearance of pesticide to 50% of its initial concentration. The residue data obtained at different intervals were subjected to statistical analysis to determine the half-life values of these insecticides on the treated substrate as per the procedure outlined by Hoskins (1961). To evaluate the risk assessment of insecticide, the TMRC was calculated by multiplying the maximum residue levels with average per capita daily consumption in the Indian context. Safety parameters were evaluated by comparing the Theoretical Maximum Residue Concentration (TMRC) with Maximum Permissible Intake (MPI) (Bhattacharya et al., 2017).

If TMRC value is less than MPI, the particular insecticide will not cause any health impact; TMRC= Maximum residue level obtained at recommended dose on 0^{th} day of application x total intake of food/ day; MPI= Acceptable daily intake x average body weight (55) kg of an adult of human being. Daily consumption value of cowpea was considered as 90 g d^{-1} (Huan et al., 2016). The prescribed ADI values of insecticides were as given by FAO/WHO.

RESULTS AND DISCUSSION

Two hours after spraying, an average initial deposit of 0.53 mg kg^{-1} was observed. On the next day 43.39% of the residues got dissipated and the level reached 0.30 mg kg^{-1}. Fruits collected on the third day recorded residue level of 0.12 mg kg^{-1} with dissipation % of 77.35 which degraded to below quantification level on fifth day and reported half-life was 1.37 days. The studies on dissipation of thiamethoxam in cowpea are scanty. Present results are more or less similar to the observations made by Singh and Kulshrestha (2005) wherein the residues persisted up to 5 days in brinjal fruits. Similarly, Allam and Singh (2016), Gupta et al. (2005) and Pathipati et al., (2018) reported persistence of thiamethoxam residues 5 days each in brinjal, gram and capsicum. In contrast to the present results, Karmakar and Kulshrestha (2009) reported that thiamethoxam persisted for about 10 days in tomato, 15 days in paddy (Barik et al., 2010) 15 days in okra (Chauhan et al., 2013), 10 days in mango (Bhattacharjee and Dikshit, 2016), 15 days in tomato (Ramadan et al., 2016). Thus, it can be concluded that variation in the rate of dissipation is due to the several factors, including the species cultivated (its crop formation physics, cuticle characteristics, growth rate, pH dependency, etc.), climatic conditions, application parameters viz., formulation, the number of applications, penetration rate, volume of water, type of nozzle, pressure, and height between the boom and the canopy (Rahman et al., 2015). ADI of thiamethoxam is 0.08 mg kg^{-1}; in cowpea fruits from 0 to 3^{rd} day after spraying was 0.53, 0.30 and 0.12 mg kg^{-1}, respectively (Fig.1- 4). Maximum permissible intake (MPI) was 4400 mg kg^{-1} bw d^{-1}, by taking 90g as daily consumption of cowpea fruits. TMRC values from 0th to 3^{rd} day after spraying were 47.7, 27.00 and 10.8µg kg^{-1} bw d^{-1}, respectively which were lower than the MPI of thiamethoxam (Table 1).

Risk assessment is the course to identify the potential menaces and the associated risks to life and health resulting from human exposure to chemicals present in food over a specific period (WHO, 2009). The use of pesticides on food crops lead to unwanted residues, which may constitute barriers to exporters and domestic consumptions when they exceed maximum residue limit. Human health risk situation are a function of hazard and exposure to that hazard. If the hazard is

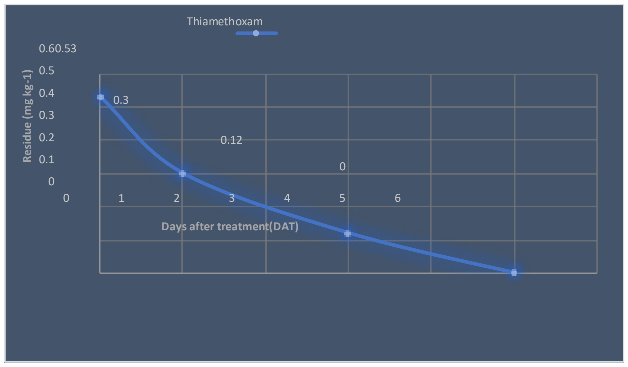

Fig 1. Dissipation of thiamethoxam in cowpea

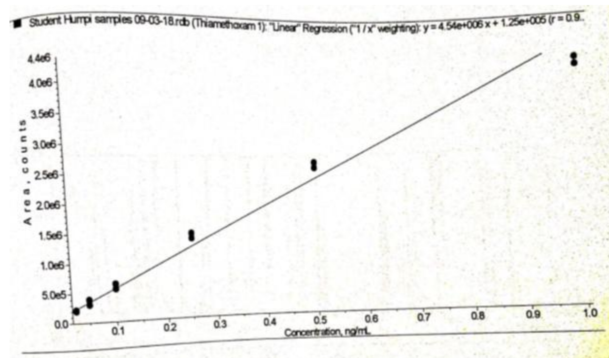

Fig 2. Calibration curve of thiamethoxam

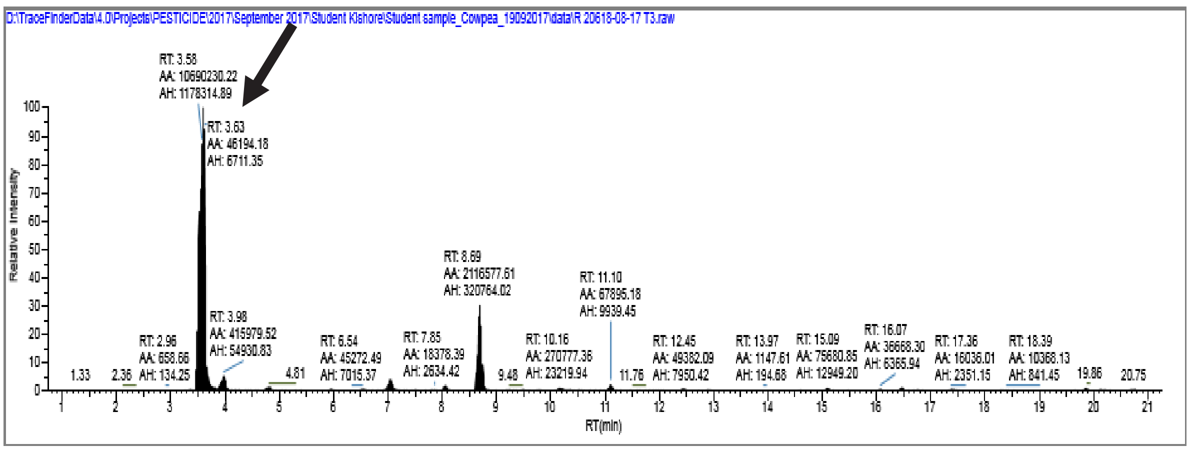

Fig 3. Chromatogram of thiamethoxam (Treatment)

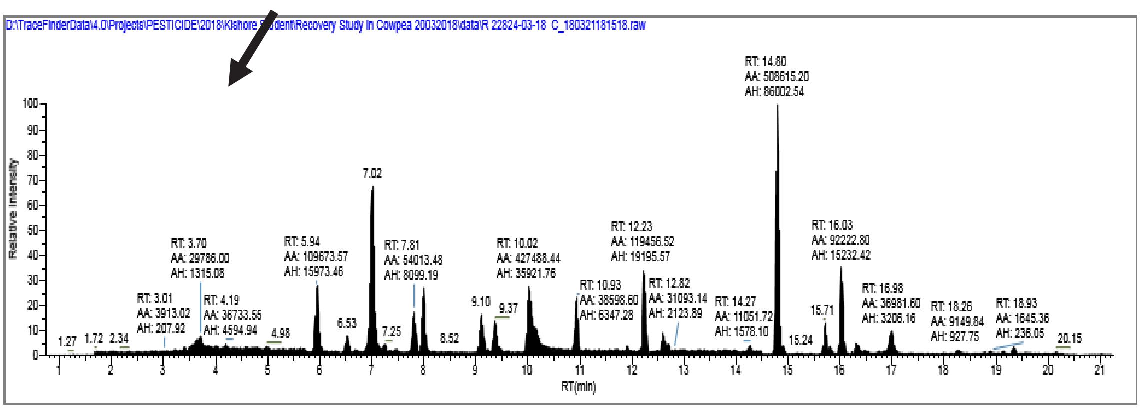

Fig 4. Chromatogram of thiamethoxam (Control)

Table 1. Risk assessment of thiamethoxam 25%WG in cowpea pods

ADI ($mg\ kg^{-1}\ bw\ d^{-1}$)	Average body weight (kg)	Interval (days)	Daily consumption rate ($g\ day^{-1}$)	MPI* ($\mu g\ person^{-1}\ day^{-1}$)	Average residue ($\mu g\ g^{-1}$)	TMRC ($\mu g\ person^{-1}\ day^{-1}$)
0.08	55	0	90	4400	0.53	47.7
0.08	55	1	90	4400	0.30	27
0.08	55	3	90	4400	0.12	10.5
0.08	55	5	90	-	BDL	-

* MPI= ADI × Average body weight × 1000

small and fixed, then the risk will be proportional to exposure, which can be reduced to low and occasional (Bates, 2002). Residue implication of foliar application of thiamethoxam on cowpea crop evaluated now by comparing theoretical maximum residue contribution (TMRC) of the pesticide with its maximum permissible intake (MPI). These results indicated that thiamethoxam did not provide any unacceptable dietary risk for consumers of cowpea across Kerala. The TMRC of thiamethoxam 25% WG was found to be well below the MPI on cowpea pods even at 2 hr of spraying. Therefore, application of thiamethoxam at the recommended dose is quite safe from crop protection and environmental contamination point of view.

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