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A REVIEW

Trends and techniques for thiamethoxam residue estimation in different vegetables and fruits

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Abstract : At this present day, the use of pesticides has become an important part of farming practices for our farmer as well as for public health. Pesticides are being used globally in such an inflated rate that many of them are on the way of becoming a serious threat to the biosphere. Besides providing a very good coverage over various pest infestations, they bring additional hazard to non-targeted organisms, application surfaces and harm to the applicator. All-round use of pesticides had resulted in tainting of all the basic necessities of life, *i.e.* air, water and food. The incessant use of pesticides has caused the deleterious effects to ecosystem as well. In response to this, numerous methods have been developed by several regulatory agencies and private laboratories which are being applied perpetually for the qualitative and quantitative quantification and monitoring of multi pesticide residues in different vegetables and crops. The main intent of the review is to document access and analyze the results of the former data on levels of different pesticides in various fruits and vegetables in India and abroad. The findings of the previous studies clearly indicated that approximately more than 50 % of the samples were contaminated with organophosphate, pyrethroids and organochlorine pesticides. Many studies reported that among fresh fruits and vegetables tomato, apple, melon, mango, grapes, and plum crossed the FAO/WHO permissible limits for these contaminants residual levels.

Key Words : Pesticides, residues, environment, QuEChERS, half-lives, Gas chromatography

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INTRODUCTION

Indian economy is greatly based on agriculture, as our country is very well known for possessing its own rich and diverse knowledge about various cultivation practices involved in agriculture. Agriculture sector supports a large portion to the nation's GDP I (Dhanker *et al.* 2020). India ranks second largest assembler of vegetable due to its excellent agro-climatic conditions for cultivation. Fruits and vegetables are the major sources of vitamins like A, B_6, C, E, thiamine, niacin etc., dietary fibres and minerals. With the view to enhance food production and prevent food insecurity the major technical evolution in 20^{th} century is the use of agrochemicals world-wide. Various forms of agricultural chemicals were developed and used to improve or protect crops and livestock hence, improving the quality of crop, saving crop losses, increasing crop productivity and reducing cost of production. And this resulted in

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enhancement in our farmer's condition economically. These agrochemicals have highly inflated the rates of food production. Thiamethoxam [3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene (nitro) amine] is a potent systemic insecticide of the rapidly growing class, Neonicotinoids (neuro-active insecticides which are chemically similar to nicotine). Analogous to nicotine, these act by binding to nerve cell receptors responding to the neurotransmitter acetylcholine. It has slight acute toxicity (LD_{50} 1530 mgkg^{-1} to rats) and fall under toxicity category III in acute oral and dermal studies. It is highly soluble in water (4.1 g L^{-1} at 25C), low partitioning coeûcient (0.74) and low vapor pressure (4.95 9 10-11 mm Hg at 25C). ADI for thiamethoxam is 0.0006 mgkg^{-1} bodyweight day^{-1} (ADI). Generally, these have a selective action on the central nervous system of insects. Additionally, these have nominal effects on valuable insects with very low mammalian toxicity, without prompting either teratogenic or mutagenic effects. Thiamethoxam acts effectively against many sucking and biting insects, like aphids, whiteflies, etc. it can be applied as foliar spray in plants as well as to the seeds. Thiamethoxam is recognized as the second biggest neonicotinoid. Thiamethoxam has been found potent against various insect sucking pests, aphids, whiteflies, beetles, thrips, lepidopterans and a number of coleopteran species. Actara and Cruiser (70 WS) are the two commercially available WG formulation of Thiamethoxam (foliar spray). There are no Codex MRLs (maximum residual limit) established for residues of thiamethoxam in tomato or other fruiting vegetables. However, list of countries which considered MRL limits are Japan (0.5 mgkg^{-1} in tomato), USA (0.2 mgkg^{-1} for okra and brinjal), Australia and New Zealand (0.02 mgkg^{-1} for maize, cotton seeds, sorghum and sweet corn), Canada (0.03 mgkg^{-1} in potato and 0.02 mgkg^{-1} in 'all other food crops'). In many cropping systems, Thiamethoxam is well suited for modern integrated pest management programmes due to its favorable safety profile, low use rates, flexible methods of application, outstanding efficacy and durable residual activity. The main aim of the review is to document, access and analyze the results of the former data on levels of different pesticides in various fruits and vegetables in India and abroad. The present review paper presents the metabolic/degradation, dissipation and persistence behavior of thiamethoxam under field/laboratory conditions in various fruit and vegetable crops like tomato, chilli, brinjal, potato, mango, okra and cabbage besides bioefficacy, when applied as a foliar spray at the fruit initiation stage.

Methods of residue estimation:

Residue Estimation by Partitioning with DCM:

Partitioning is one of the most commonly used and efficient method for residue analysis. For residue analysis, fruit samples of 0.5 kg were collected randomly at the periodic intervals of 0 (1h after treatment), 1, 3, 5, 7 and 15 days after treatment along with control. The samples collected are carried to laboratory and chopped. Chopped samples are triplicated and 20g sample are extracted with 80 ml acetone followed by mechanical shaking for 1 h. The extracts are filtered and transferred to separatory funnel. Later these are diluted with 10 % aqueous solution of NaCl and partitioned thrice with dichloromethane, DCM (50, 30, 20 ml). The dichloromethane phase is passed through anhydrous sodium sulphate and by using rotary vacuum evaporator sample is concentrated upto 5 ml. By using column chromatography, fruit extract are cleaned. In between two layers of anhydrous sodium sulphate glass column (60 cm × 22 mm i.d.) packed with 0.3 g activated charcoal and 5 g silica gel. The glass column is eluted with 125 ml hexane: acetone in ratio of 9:1. The remnant was concentrated to near dryness on rotary vacuum evaporator and made the final volume to 2 ml in n-hexane. The residues are estimated using gas liquid chromatograph (GLC). Wang *et al*. (2013), Karmakar and Kulshreshtha (2009), Barik *et al.* (2010), and Chauhan *et al.* (2013) conducted their experiments on different fruits and veggies using liquid-liquid portioning. Similar method of partitioning was also used by Bhatterjee *et al*. (2016) with slight modifications. Thiamethoxam (Actara® 25 WG) at 0.2 and 0.4 g L^{-1} water (0.008 and 0.016 %) was sprayed during the fruit development stage on respective crops. There was random collection of samples at 0 (2h after spraying),1,3,5,7,10,15,20,25,30, and 40 days after spraying. 20 g of fruit samples (in triplicate) were homogenized, they were extracted with 50+50 mL acetonitrile in a vertical homogenizer after soaking overnight followed by filtration through a Buchner funnel. Evaporation of acetonitrile near to dryness was carried under vacuum in a flash vacuum evaporator at 50 °C. The remnant was transferred into a 250-mL separating funnel and after diluting with 50 mL sodium chloride solution (15 %) it was extracted with hexane (thrice,3×30 mL). The hexane layer was casted off and partitioning of aqueous layer was carried out three times with dichloromethane (3×30 mL). Drying of pooled dichloromethane extract through anhydrous sodium sulfate followed by complete evaporation in a flash vacuum evaporator (40 °C). Estimation and reconstitution of residue is finalized by using 2-mL HPLC-grade acetonitrile.

Residue Estimation by QuEChERS:

The method of QuEChERS (quick, easy, cheap, effective, rugged, and safe) was introduced by Anastassiades *et al.* (2003). For extraction, 20 g of fruit samples was taken in a centrifuge tube (50 mL capacity), followed by addition of 5 mL of acetonitrile and 15 mL of water. After that 7 g of NaCl and 8 g of anhydrous $MgSO_4$ were added to the sample. Contents were shaken vigorously for 5 minutes. Thereafter, the samples were placed on a horizontal shaker for 1 hours at 250 rpm. The mixture was centrifuged at 5000 rpm for 5 min. After this, phase separation occurs and the upper layer of acetonitrile was collected without disturbing lower layer, with the help of micropipette. Thereafter, the cleanup step was carried out by filtration through a column containing anhydrous sodium sulphate to remove the moisture content. Methanol was used as an eluent. The drying of eluted methanol was carried under the stream of nitrogen and re-dissolved in mobile phase (1ml) for HPLC analysis. The samples were filtered through 0-disc filter (45 μm Millipore) prior to injection into the HPLC system.

Olway *et al.* (2016) performed an experiment by using QuEChERS method on brinjal. Recovery experiment was performed at different fortification levels 0.01, 0.05, 0.10, 0.20 (mg kg$^{"1}$) and the recorded percentage recoveries were 80.17, 80.97, 97.3, 97.8 respectively. At two different doses i.e. @ 50 g a.i. ha^{-1} and 100 g a.i. ha^{-1}, dissipation was 91.6 and 90.4 % and fell below detection level (BDL) on 10th day. As per first order kinetics half life time value were observed to be 2.57 and 2.28 respectively on different application rates. Bhattacherjee *et al.* (2016) anlysed the residues of thiamethoxam on mango crop with 92.6 and 96.00 % percentage recoveries at different fortification levels *i.e.* 0.4 and 0.1 (mg kg^{-1}). Residues were estimated by partitioning method and the data revealed that dissipation of residues in mango fruit is from 1.93 and 3.71 mg kg $^{"1}$ after 2 h of spraying to 0.08 and 0.13 mg kg$^{"1}$ after 20 days of spraying at different application rates *i.e.* (0.008 and 0.016 %) respectively). 96 % dissipation was observed after 20 days of spraying. It fell BDL after 25 days. By following first order kinetic equation half life time period observed is 4.5 and 4.0 days at normal and higher doses, respectively. Kumar *et al.* (2014) detected the thiamethoxam residue in potato crop using QuEChERS method for estimation of residues. Recovery studies were performed at different fortification levels i.e. 12.5 and 25 μg/g with percentage recovery of 82 and 83% respectively. On 90 days after planting no residues of thiamethoxam (< 0.05 μg/g) were detected on both application rates (25 and 50 g/thiamethoxam). From the respective data it is concluded that for environment and human consumption thiamethoxam is safer to use. Chauhan *et al.* (2013) estimated the residues of thiamethoxam on okra by using partitioning method performed under laboratory conditions. The average initial deposit of thiamethoxam was detected to be 0.245 mg kg^{-1}. On 1, 3 and 7 days after application, depositions observed were 0.158, 0.097 and 0.009 mg kg^{-1} or in terms of percentage dissipation 35.51, 60.40, 96.32 on the respective days. Thiamethoxam residues fell below detectable level on 15th day (0.005 mg kg^{-1}). So concluded the less persistence nature of this insecticide. Observed half-life period is 1.47 days and followed the kinetics of first order. Same results were shown by Pramanik *et al.* (2015) and Reddy *et al.* (2016). Barik *et al.* (2010) performed the experiment on residue estimation of thiamethoxam by partitioning method on paddy plant and the average recovery of thiamethoxam was 88.0%. Residue estimation of thiamethoxam was performed at initial deposits (2 h after spraying) found to be 0.50 ìg g^{-1} (T_1) and 0.83 ìg g^{-1} at double (T_2). No residue was detected in the untreated control (T_3) samples of paddy plant. After 5th day of application ,40%–60% dissipation is observed followed by 83%–88% after 15 days irrespective of the application doses. The dissipation of thiamethoxam followed first order reaction kinetics and the half-life values of thiamethoxam is 5.2 days for T_1 and 5.8 days for T_2. Hem *et al.* (2010) examined the residues of thiamethoxam in pomegranate were lower than its MRL value (0.5 mg kg^{-1}) established by the Korea Food and Drug Administration. Karmakar *et al.* (2009) also anlysed the residues of thiamethoxam on tomato crop. Partitioning was performed with hexane followed by DCM. At different fortification levels *i.e.*

0.2, 0.5 and1 μg g^{-1} percentage recovery were 86, 92 and 91%, respectively. At the time of fruiting, tomato fruit samples were sprayed with thiamethoxam and anlysed at 0 (3 h), 1, 3, 5, 7, 10 and 15 days after the application. On application of 140 and 280g a.i. ha^{-1} of thiamethoxam, the initial deposits of 0.182 and 0.303 $mgkg^{-1}$, respectively were observed with a very rapid dissipation of residues. 49 and 30% dissipation was observed on day 3 after two rates application, respectively. 59 and 72% dissipation was recorded on days 5 and 7 at the normal rate followed by 49 and 65% at the higher dose. There is further dissipation of residue *i.e.* 82 and 88% on 10^{th} day, and fell below the detectable level on 15^{th} day. First order kinetics was followed by dissipation of thiamethoxam with half-lives of 4.2 and 3.5 days, respectively at two application rates. Singh *et al.* (2009) examined apple samples collected from integrated pest management and non-integrated pest management orchards and observed after harvesting and found free from thiamethoxam residues. Venkateswarlu *et al.* (2007) anlysed the concentration of thiamethoxam residues in grape samples, collected from an agricultural field of Hyderabad, India. He observed that the residue was present in a permissible limit. Singh *et al.* (2005) performed the experiment using partitioning with hexane followed by DCM w.r.t. residue estimation of thiamethoxam on okra fruit and anlysed the average recovery of chemical *i.e.* 84%. First application of pesticide is performed at flowering stage and no residues were detected. In the 2^{nd} experiments insecticide application (140 and 75 gm a.i ha^{-1}) was performed at flowering as well as fruiting stage and the samples were anlysed on 0 (3 h), 1, 3, 5 and 7 days after the application. They observed 50 % dissipation on 3^{rd} day followed by 95.5 % on 5^{th} day and the residues were below detectable limits after 7^{th} day of application. This results followed the first order kinetics and half-life of 1.3 days.

Conclusion:

By documentation and analysis of the results of the former data on levels of different pesticides in various fruits and vegetables in India and abroad analyzing the of various research papers concluded that the dissipation and persistence behaviour of thiamethoxam on various crops like okra, mango, tomato, apple, pomegranate, potato, brinjal etc. for controlling pests, were found to be toxicologically acceptable when applied at the fruit development stage. The fruits can be consumed safely after pre-harvest intervals of 7 and 11 days.

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