IJFANS
International Journal of Food And Nutritional Sciences

Volume 4, Issue 3, Apr-Jun 2015, www.ijfans.com e-ISSN: 2320-7876

INTERNATIONAL JOURNAL OF FOOD AND NUTRITIONAL SCIENCES

IMPACT FACTOR ~ 1.021

Official Journal of IIFANS

INTERNATIONAL JOURNAL OF FOOD AND NUTRITIONAL SCIENCES

e-ISSN 2320 –7876 www.ijfans.com
Vol.4, Iss.3, Apr-Jun, 2015
All Rights Reserved

Research Paper *Open Access*

DISSIPATION AND RISK ANALYSIS OF DIMETHOATE IN OPEN FIELD AND POLY HOUSE TOMATO AND RISK MITIGATION METHODS OF REMOVAL OF DIMETHOATE RESIDUES FOR FOOD SAFETY

Sudhakar. S. Kelageri[1], Cherukuri Sreenivasa Rao[1*], Shashi. V. Bhushan[1] and Narayana. P. Reddy[2]

[1]All India Network Project on Pesticide Residues, ANGR Agricultural University, Hyderabad, India, [2]Department of Plant Pathology, College of Agriculture, Rajendranagar, ANGRAU, Hyderabad, India

[*]Corresponding author: cherukurisrao@yahoo.com

Received on: 28th January, 2015 **Accepted on: 18th June, 2015**

ABSTRACT

Dimethoate is a widely used insecticide on Tomato in India for the management of sucking and leaf eating insect pests in both open field and poly houses. Dissipation and risk analysis of dimethoate in two situations was carried out at recommended dose i.e. Dimethoate 30% EC @ 300 g a.i. ha^{-1} and tomato fruits were analyzed at regular interval till the residues are below determination level (BDL) of 0.05 mg kg^{-1} following the validated QuEChERS method, analysis on GC-FPD and confirmation on GC-MSMS (TQD). Initial deposits of 1.31 mg kg^{-1} were detected in samples collected from open field, which dissipated to BDL by 7th day, and in poly houses, deposits of 1.76 mg kg^{-1} dissipated to BDL by 10th day, with half-life of 1.55 and 1.63 days, respectively, reveal that dissipation is slow in poly house. MRLs of 3 mg kg^{-1} and 4 mg kg^{-1} recommended in open field and poly house, respectively, as per OECD MRL calculator and chronic hazard exposure assessment since the theoretical maximum daily intake is less than calculated MRLs based on per capita tomato consumption and average body weight. Among various decontamination methods tested, veggy wash found to be very effective in removing dimethoate residues to an extent of 76.77 %, followed by 4% acetic acid solution (65.49 %) and tap water wash was least effective (23.29 %) in removing dimethoate residues from tomato.

Key words: Tomato, dimethoate, poly house, open fields, dissipation, risk analysis, risk mitigation methods.

INTRODUCTION

Tomato (*Lycopersicon esculentum* Mill.) is one of the most important vegetable crops in India grown commercially both in open fields during seasons and poly house in controlled environments during off-seasons. It is most widely consumed vegetable usually in the form of curry, and also in raw form as salad, home-cooked, or processed as juice, paste, or sauce. Tomato contains 200 kcal kg^{-1}, 9 g protein kg^{-1}, and 2 g fat kg^{-1} (Gopalan et al. 1991). Per capita consumption of tomato in India increased from 7.8 kg in 2008 to 12.2 kg in 2011 (FAO stat). During 2012-13 in India, tomato was cultivated in an area of 879.6 thousand ha with an average annual production of 18226.6 thousand t and productivity of 20.7 t ha^{-1}, which contributed about 9.6% of total vegetable area and 11.2% of total vegetable production (Indian horticulture database 2014). The tomato yield in India is considerably lower because of several factors of which the damage caused by leaf hoppers, aphids, caterpillar, flea beetles, leaf miner, spider mites, and fruit borer (Singh et al. 1989) is economical, and of which fruit borers such as *Helicoverpa armigera* and *Spodoptera litura* cause severe losses to farmers. The synthetic pesticides are the important tool in pest management, but their unguided use cause severe ecological consequences like destruction of natural enemy fauna, effect on non-target organisms, secondary pest outbreaks, and food safety issues like presence of pesticide residues in food which may lead to deleterious impacts in long run not only on human health but also on other biota. Central Insecticide Board and Registration Committee of India registers and recommends various pesticides for pest management, and in tomato, out of all recommended pesticides, dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate), an organo phosphate insecticide, is the most commonly used against both sap sucking and chewing insects due to its systemic, contact and acaricidal action. Dimethoate 30% EC is recommended @ 200 g ai ha^{-1} against aphids in open field condition (cibrc.nic.in) and based on survey it is documented that farmer's use @ 300 g ai ha^{-1} in open field and poly house conditions, which is higher than recommended dose. It is moderately toxic with acceptable daily intake of 0.002 mg kg^{-1} day^{-1} and hence risk analysis is essential for recommending MRLs as per changed GAPs (Good Agricultural Practices). Indian Maximum Residue Limits (MRLs) for dimethoate for vegetables are 2 mg kg^{-1}

(Food Safety and Standards Regulation, 2011) and there are no MRLs for tomato as per Codex Alimentarius Commission. A study was conducted during 2012-13 crop seasons (kharif) to assess the dissipation dynamics of dimethoate on tomato in two commonly growing situations (open field and poly house farming practices) so as to recommend MRLs, pre harvest intervals based on MRL calculated using OECD (Organization for Economic Co-operation and Development) MRL calculator and Theoretical Maximum Daily Intake (TMDI), a chronic hazard exposure assessment indicator. Studies also conducted to establish the recommendations for removal of dimethoate residues from tomato with simple house hold techniques for food safety.

MATERIALS AND METHODS

Certified Reference Material of dimethoate (99.6% purity) was procured from M/S Sigma Aldrich, Germany, and Dimethoate 30% EC was obtained from M/S Rallis India. Primary, intermediary and working standards were prepared from the CRMs using acetone and hexane as solvents. Working standards of all the pesticides were prepared in the range of 0.01 ppm to 0.5 ppm in 10 mL calibrated graduated volumetric flask using distilled n-hexane as solvent, and injected in Gas Chromatograph with Electron Capture Detector (ECD) and Thermionic Specific Detector (TSD) for estimating the lowest quantity of dimethoate can be detected with injector split ratio of 1:10 (GC- Agilent 7890B, VF-5ms Capillary Column, ECD and TSD) and the same was confirmed on Bruker Scion GC-MS/MS (TQD) using MRM method, and it was found that the LOD (limit of detection) for dimethoate is 0.01 ng, and the linearity is in the range of 0.01 ng to 1 ng. Prior to field and poly house experiments to study the dissipation dynamics, QuEChERS method (Anastassiades *et al*., 2003) for extraction and clean up was validated as per SANCO/12495/2011 guidelines. Tomato fruits (5 kg) were collected from untreated control plots and the stalks were removed prior to samples preparation. The sample was homogenized using Robot Coupe Blixer (High volume homogenizer) and 15 g was taken in to 50 mL centrifuge tubes. The required quantity of dimethoate intermediary standard is added to each 15 g sample to get fortification levels of 0.05 mg kg^{-1}, 0.25 mg kg^{-1} and 0.5 mg kg^{-1} in three replications each. 30±0.1 mL acetonitrile was added to the tube, and sample was homogenized at 14000-15000 rpm for 2-3 min using Heidolph silent crusher (low volume homogeniser). Then 3±0.1g sodium chloride was added to tube and mixed by shaking gently, and centrifuged for 3 min at 2500-3000 rpm to separate the organic layer. The top organic layer of about 16 mL was taken into the 50 mL centrifuge tube to which 9±0.1 g anhydrous sodium sulphate was added to remove the moisture content. 8 mL of extract was taken in to 15 mL tube containing 0.4±0.01g PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2±0.01 g anhydrous magnesium sulphate, and the sample tube was vortexed for 30 sec followed by centrifugation for 5 min at 2500-3000 rpm. The extract of (2mL) was transferred into test tubes and evaporated to dryness using turbovap with nitrogen gas and reconstituted with 1mL n-Hexane: Acetone (9:1) for dimethoate analysis. Tomato samples fortified with dimethoate at 0.05 mg kg^{-1}, 0.25 mg kg^{-1} and 0.5 mg kg^{-1} were analyzed and the mean recovery of the residues using the method was 99.23%, 94.68% and 88.27%, respectively (Table 1). The results showed that the method is suitable for the analysis of dimethoate residues up to 0.05 mg kg^{-1}, and the limit of quantitation (LOQ) is 0.05 mg kg^{-1}.

Table 1 - Recovery of dimethoate residues from tomato

Replication	Fortified level (mg kg^{-1})					
	0.05 mg kg^{-1}		**0.25** mg kg^{-1}		**0.50** mg kg^{-1}	
	Residues recovered (mg kg^{-1})	**Recovery %**	**Residues recovered (mg kg^{-1})**	**Recovery %**	**Residues recovered (mg kg^{-1})**	**Recovery %**
R1	0.050	100.80	0.244	97.71	0.446	89.15
R2	0.053	105.20	0.232	92.78	0.433	86.68
R3	0.046	91.70	0.234	93.55	0.445	89.00
Mean		99.23		94.68		88.27
SD		6.907		2.652		1.379
RSD		6.961		2.801		1.563

Tomato crop (Popular hybrid Nirupama) was raised in both poly house and open field laid out in Randomized Block Design at spacing of 60×45 cm with each plot size of 20 m^2 and all Good Agricultural Practices (GAPs) recommended by University were followed. Dimethoate was sprayed @ 300 g a.i. ha^{-1} twice; first spray at fruit initiation stage followed by second spray at 10 days after first spray, using high volume knapsack sprayer with a spray solution of 500 L ha^{-1}. Pest damage free and crack free tomato fruits of 5 kg were collected in separate polythene bags at regular intervals i.e. 0, 1, 3, 5, 7, 10, 15, 20 days after last spray for dissipation studies. Half-life and TBDL (time required for residues to reach below determination level) were calculated as per Hoskins (1966) from first-order dissipation kinetics. OECD MRL calculator is used for calculation of MRL and chronic hazard risk analysis was performed using TMDI (Theoretical Maximum Daily Intake) for arriving at MRL for recommendation.

For evaluation of risk mitigation / decontamination methods, zero day samples were collected separately in large quantities and made into six sets, each in four replications. One set of sample is analyzed for initial deposits of dimethoate. The remaining sets of samples were subjected to various decontamination methods separately and the residues were calculated to know the efficiency of the various decontamination methods in removal of pesticide residues from the tomato samples. The decontamination / risk mitigation methods selected for evaluation of efficiency in removal of pesticide residues from tomato were presented in Table 2. After decontamination treatments, the samples were shade dried for 10 min placing on clean blotting papers and analysed for residues remaining on tomato. The per cent dimethoate residues removed from samples is calculated.

RESULTS AND DISCUSSION

The fortification and recovery results (Table 1) showed that the limit of determination for dimethoate residues in tomato is 0.05 mg kg^{-1} with a recovery of 99.23 $\pm$ 6.91%. The field data on dissipation dynamics of dimethoate from studies conducted in open field and poly house situation are presented in Table 3 and Fig 1. In open field situation, initial deposits of 1.31 mg kg^{-1} dimethoate were detected at 2 hours after last spray, which dissipated to 0.62, 0.47 and 0.12 mg kg^{-1} and Below Determination Level (BDL) of 0.05 mg kg^{-1} by 1, 3, 5 and 7 days after last spray, respectively. MRL of 3 mg kg^{-1} is suggested as per OECD MRL calculator, and half-life of 1.55 days, and TBDL of 11.85 days is calculated. Taking into consideration of MRL of 3 mg kg^{-1} and chronic hazard exposure assessment parameters such as per capita consumption of tomato and average body weight, theoretical maximum daily intake of 0.00147 mg kg^{-1} bw calculated is less than ADI of 0.002 mg kg^{-1} bw (Table 4). Hence MRL of 3 mg kg^{-1} and PHI of 1 day is proposed in the changing scenario of GAP, as the existing FSSAI MRL of 2 mg kg^{-1} for fruits and vegetables is recommended based on the registered use of dimethoate 30% EC on tomato @ 200 g ai ha^{-1}. In poly house conditions, initial deposits of 1.76 mg kg^{-1} dimethoate detected at 2 hours after last spray, dissipated to 1.14, 0.55, 0.20, 0.09 mg kg^{-1} and BDL by 1, 3, 5, 7 and 10 days after last spray, respectively. The dissipation pattern showed decrease of residues from first day to 10^{th} day and the residues dissipated by 35.22, 68.75, 88.63 and 94.88 % at 1, 3, 5 and 7 days, respectively. There are no Maximum Residue Limits (MRLs) for dimethoate as per Codex Alimentarius Commission (CAC), while Food Safety and Standards Authority of India (FSSAI) suggest MRL of 2 mg kg-1 for fruits and vegetables grown under normal field conditions. The dissipation is slow in poly house conditions as the half-life is 1.63 days. Based on the present investigation, MRL of 4 mg kg^{-1} is suggested for dimethoate on poly house tomatoes as the TMDI (0.00196 mg kg^{-1} bw) is less than ADI (0.002 mg kg^{-1} bw), and a pre harvest interval of 1 day can be recommended for food safety (Table 4). Gajbhiye et al. (1994) reported that dimethoate when sprayed @ 360 g a.i. ha^{-1} on bottle guard, bitter gourd and musk melon recorded initial deposit of 1.20, 1.15 and 1.10 mg kg^{-1}, respectively which dissipated to Below Determination Level (BDL) by 7^{th} day in all three crops, safe waiting period of 3 days was suggested in all three crops. The trials conducted on okra spraying dimethoate @ 0.06% recorded initial deposit of 2.93 mg kg^{-1} and the PHI (Pre-Harvest Interval) of 2 days is suggested by Khan, 1997. Although studies were conducted on dimethoate dissipation dynamics on various crops, but no studies were conducted in poly house situations. However, it can be attributed that the dissipation is slow in poly houses compared to open fields due to very common factors such as cool climatic conditions and less sun light penetration in poly house. The studies are very helpful for the fixation of MRLs and recommendation of MRLs based on the dose recommendations of dimethoate in poly houses / controlled environmental conditions.

The data on efficacy of decontamination methods on tomato fruits for removal of dimethoate residues is presented in Table 5. The percentage removal of dimethoate residues in tomato when subjected to different decontamination solutions at 2 hours after spraying showed that dipping in veggy wash solution for 10 min followed by tap water wash for 10 sec was found to be most effective removing 76.77% dimethoate residues than other treatments. The next promising method is 4% Acetic acid solution (65.49 %), followed by 2% salt solution (58.69 %), 0.1% baking soda solution (52.30 %) and tap water (23.29 %). In the present study, veggy wash, a formulation prepared by AINP on Pesticide Residues, Hyderabad proved to be the most efficient in removing various pesticides. Mohamed H. Shiboob et al. (2014) reported that dimethoate residues were removed to an extent of 65.21% due to 2% acetic acid, 54.23% due to 1% salt solution, 60.70% due to 1% soap water, 97.32% due to 0.01% potassium permanganate and 82.54% due to tap water washings in tomato. Washing of hot pepper, sweet pepper and brinjal with 2% acetic acid removed pirimophos-methyl residues by 76.61, 95.74 and 94.58 % (Radwan MA et al. 2004). Similarly, Zhang et al (2007) found that 79.8, 65.8, 74.0 and 75.0% residues of chlorpyrifos, *p,p*-DDT, cypermethrin and chlorothalonil were removed by washing cabbage with 10% acetic acid solution for 20 min, respectively. Dipping of tomatoes in 0.1% baking soda ($NaHCo_3$) solution for 10 min also removed dimethoate residues, and are in line with the findings of Liang et al (2012) who reported that washing of cucumber with 2% $NaHCO_3$ was efficient enough to remove the trichlorfon, dimethoate, dichlorovos, fenitrothion and chlorpyrifos residues by 73.20, 58.70, 96.40, 51.10 and 77.80%, respectively. Tap water wash was the least effective treatment and the findings of present investigations are in agreement with the findings of Abou-Arab (1999) who reported that washing of tomato fruits with water removed dimethoate and profenophos residues up to 18.80 and 22.17 % respectively. Results of the present investigations indicate that simple house hold techniques can be used for removal of pesticide residues from tomato, especially when used as salads to reduce the risk of pesticide contamination.

Table 2 -Decontamination Methods for removal of dimethoate residues from tomato

S.No	Treatment	Details of treatment
T1	Tap water wash	4 L of tap water was taken into the plastic tub of 7 L capacity and 2 Kg of tomato fruits were dipped in the tub for 10 min, followed by the tap water wash for 10 sec.
T2	Soaking in 2% salt solution	4 L of 2 % salt solution was prepared by mixing 80 g of table salt in 4 L of water in plastic tub of 7 L capacity and 2 Kg tomato fruits were dipped in the tub for 10 min, followed by the tap water wash for 10 sec.
T3	Dipping in 0.1% baking soda) ($NaHCo_3$)	4 L of 0.1% baking soda solution was prepared by mixing 4 g of baking soda in 4 L of water in plastic tub of 7 L capacity and 2 Kg tomato fruits were dipped in the tub for 10 min, followed by the tap water wash for 10 sec.
T4	Soaking in 4% acetic acid solution	4 L of 4% acetic acid solution was prepared by mixing 160 ml of acetic acid glacial 100% in 4 L of water in plastic tub of 7 L capacity, mixture was kept for 1 min and 2 Kg of tomato fruits were dipped in the tub for 10 min, followed by the tap water wash for 10 sec.
T5	Veggy wash	4 L of veggy wash was prepared by mixing 160 ml of acetic acid glacial 100%, 4 g of baking soda and lemon juice of 4 lemons in 4 L of water in plastic tub of 7 L capacity, mixture was kept for 1 min and 2 Kg tomato fruits were dipped in the tub for 10 min, followed by the tap water wash for 10 sec.

Table 3 - Dissipation of dimethoate residues in open fields and poly house situations

Days after treatment	Residues in Open field (mg kg^{-1})						Residues in Poly house (mg kg^{-1})					
	R1	R2	R3	R4	Mean±SD	% dissipation	R1	R2	R3	R4	Mean±SD	% dissipation
0 (2 h)	1.31	1.33	1.31	1.31	1.31±0.0112	0	1.81	1.77	1.65	1.80	1.76±0.0758	0
1	0.62	0.62	0.63	0.61	0.62±0.0078	52.67	1.16	1.14	1.14	1.12	1.14±0.0177	35.22
3	0.46	0.48	0.46	0.48	0.47±0.0091	64.12	0.56	0.54	0.56	0.56	0.55±0.0106	68.75
5	0.14	0.14	0.11	0.11	0.12±0.0179	90.83	0.20	0.19	0.20	0.20	0.20±0.0017	88.63
7	BDL	BDL	BDL	BDL	BDL	100	0.08	0.09	0.09	0.09	0.09±0.0052	94.88
10	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL	BDL	BDL	100
Regression equation (log*1000 residues)	Y = 3.094+ (-0.194) X						Y = 3.253+ (-0.185) X					
R^2	0.919						0.997					
Half-life (Days)	1.55						1.63					
TBDL (Days)	11.85						12.43					

BDL Below Determination Level of 0.05 mg kg^{-1}

Table 4 -Chronic hazard exposure assessment for recommending dimethoate MRLs on tomato in open field and poly house farming situation

OECD MRL calculator Date sets	Open field	Poly house
Total number of data (n)	5	5
Percentage of censored data (%)	20	0
Number of non-censored data	4	5
Lowest residue	0.040	0.090
Highest residue	1.310	1.760
Median residue	0.470	0.560
Mean	0.510	0.750
Standard deviation (SD)	0.509	0.698
Correction factor for censoring (CF)	0.867	1.000
Proposed MRL estimate	**Poly House**	**Open Field**
Highest residue	1.310	1.760
Mean X 4 SD	2.544	3.540
CF X 3 Mean	1.326	2.250
Unrounded MRL	2.544	3.540

Rounded MRL	3	4
Risk Analysis	**Poly House**	**Open Field**
Average human body weight (kg)	55	
National per capita intake of tomato	806 g month^{-1}	
Daily intake of crop (C) = kg person $^{-1}$	0.027	
Consumption of crop C(F_C) = kg kg bw^{-1}	0.00049	
ADI for Dimethoate (mg kg bw^{-1})	0.002	
TMDI = F_c X MRL (from OECD calculator)	0.00147	0.00196
TMDI v/s ADI	TMDI < ADI	TMDI < ADI
Proposed MRL (mg kg^{-1})	**3**	**4**

Table 5 - Removal of Pesticide Residues from Tomato fruits with different decontamination methods

Treatments	Mean of dimethoate detected (mg kg^{-1})*	Amount removed (mg kg^{-1}) **	Percent removed
Tap water wash	1.01$\pm$0.109	0.31$\pm$0.061	23.29
2% salt solution	0.54$\pm$0.021	0.77$\pm$0.043	58.69
0.1% baking soda solution	0.63$\pm$0.042	0.69$\pm$0.072	52.30
4% acetic acid solution	0.45$\pm$0.032	0.86$\pm$0.091	65.49
Veggy wash	0.31$\pm$0.049	1.01$\pm$0.099	76.77

C. D. at 5% = 1.55
Initial deposit = 1.31mg kg^{-1},
* Mean of three replications
** Amount removed = Initial deposit-Mean of replicates of each treatments.

CONCLUSIONS

As per the Insecticide Act, dimethoate 30 % EC is registered and recommended for use on tomato @ 200 g ai ha^{-1} with a MRL of 2 mg kg^{-1} for fruits and vegetables. Tomato growers in open field and poly houses spray dimethoate @ 300 g ai ha^{-1} for insect pest management. The dissipation and risk analysis studies on dimethoate on tomato conducted reveals that MRL of 3 mg kg^{-1} and 4 mg kg^{-1} in open field and poly houses can be suggested based on OECD MRL calculator and chronic hazard risk assessment taking into consideration of per capita tomato consumption and ADI, with a pre harvest interval of 1 day for food safety. Dimethoate residue can be removed by simple washing with veggy wash and 4% acetic acid solution for safe food consumption.

REFERENCES

- Abou-Arab AAK (1999) Behavior of pesticides in tomatoes during commercial and home preparation. Food chemistry 65(4): 509-514.
- Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86(2):412-431.
- Faostat.fao.org
- Food Safety and Standards (Contaminants, Toxins and Residues) Regulation (2011) of Food Safety and Standards Authority of India.
- Gopalan C, Ramasastry BV, Balasubramanian SC (1991) Nutritive Values of Indian Foods. National Institute of Nutrition, Hyderabad, India.
- Indian horticulture database (2014). National Horticultural Board. February 2014. 181-185.
- Liang Y, Wang W, Shen Y, Liu Y and Lui XJ (2012) Effects of home preparation on organophosphorus pesticide residues in raw cucumber. Food Chemistry 133(1): 636-640.
- Method validation and quality control procedures for pesticide residues analysis in food and feed. SANCO/12495/2011. European Commission Health and Consumer Protection Directorate-General.
- Mohamed H Shiboob, Mohamed H Madkour, Ahmad A Zaitoun (2014) Effect of washing and household processing on removal performances of some organophosphorus insecticides. J Food, Agri and Env 12(2):1255-1259.
- Radwan MA, Shiboob MM, Elamayem A and Aal AA (2004) Pirimiphos-methyl residues in some field grown vegetables and removal using various washing solutions and kitchen processing. Int J Agri and biol 6(6):1026-1029.
- Singh B, Singh PP, Battu RS, Kalra RL (1989) Residues of synthetic pyrethroid insecticides on tomato under sub-tropical conditions of Punjab, India. Bull Environ Contam Toxicol 43 (5): 733–736.
- www.cibrc.nic.in
- Zhang ZY, Liu XJ and Hong XY (2007) Effects of home preparation on pesticide residues in cabbage. Food Control 18(12): 1484-1487.