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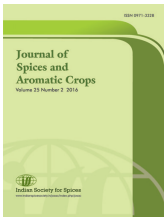

Degradation of monocrotophos in cardamom under field conditions and during processing

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Abstract

The degradation pattern of monocrotophos (Dimethyl (E) -1- methyl-2-(methyl carbamoyil) vinyl phosphate) in small cardamom (*Elettaria cardamomum*) under field conditions and during processing were studied. Monocrotophos 36% SL was sprayed at the recommended dose of 0.072% as per standard foliar application procedures. The residues were determined by gas chromatography with flame photometric detector. The degradation of monocrotophos followed first order kinetics and the half life of monocrotophos in fresh cardamom capsules was found to be five days. Due to dehydration during processing of fresh cardamom capsules, monocrotophos residue in cardamom capsule was found to be magnified by 3.5 times. Monocrotophos residue was reduced by 11.5% on curing and 29.5% on polishing.

Keywords: cardamom, degradation, half life, monocrotophos, MRL, processing

Small cardamom (*Elettaria cardamomum* Maton) is known as the queen of spices. It is the dried fruit of a herbaceous perennial plant belonging to the ginger family, Zingiberaceae. Thrips, borers, root grubs, shoot flies *etc*. are the major pests often found in nurseries and plantations of cardamom causing varying degrees of crop damage (Thomas 2001). Infestation of borer on capsule, panicle and shoot is a serious problem on cardamom in Kerala, Tamil Nadu and Karnataka (Spices Board 2009). The pest is the larva of a lepidopteran, *Conogethes* (*Dichocrocis*) *punctiferalis* (Guen.) of Crambidae family in cardamom. Insecticide sprays at late stages of the larvae which bore in pseudostem may not give adequate control of the pest. For an effective management, the insecticide has to be targeted on early stages of the larvae, which are usually present on panicles/ racemes within 15-20 days after adult emergence in the field. Injection of insecticide/*Bacillus thuringiensis* (Biological insecticide) solution through the bore hole is also a method for controlling larvae in pseudostems. Monocrotophos [Dimethyl (E) -1-methyl-2-(methyl carbamoyil) vinyl phosphate] belonging to organophosphate group of pesticides is used for managing shoot and capsule borer. Monocrotophos is classified under class Ib (highly hazardous) of pesticides (WHO 2009). Prolonged oral intake of monocrotophos, probably through food exacerbates the glucose and lipid homeostasis;

causes oxidative stress and ultimately leads to cardiotoxicity to humans (Velmurugan *et al.* 2012). Monocrotophos is a registered pesticide in India (Central Insecticides Board & Registration committee 2011), but is banned in Kerala (Kerala Agricultural University 2011). For cardamom, however farmers of Tamil Nadu and Karnataka are still using this chemical where it is not banned. Pesticide residues in small cardamom need to be kept below MRL through Good Agricultural Practices (GAP). Pre harvest interval (PHI) needs to be worked out for each pesticide used in cardamom. An experiment with an objective to study the persistence of monocrotophos in cardamom under field conditions and after processing was undertaken at Indian Cardamom Research Institute, Spices Board, Myladumpara, Idukki, Kerala (9°53′N × 77°9′E) from February 2011 to April 2011. Monocrotophos 36% SL sprayed at the recommended dose of 0.072% (Spices Board 2009) by using manually operated mist blower. Total volume of spray solution was two liters per plant. Spraying was carried out on 2nd February 2011 in nine year old plantation. 100 bearing clumps of cardamom were tagged for the study.

The fresh cardamom samples were collected for pesticide residue estimation on 1, 3, 5, 7, 9, 12, 14, 16, 18, 20, 22, 25, 27, 30, 33, 36 and 39 days after spraying of monocrotophos randomly. One hundred grams sample was harvested randomly from each harvest for the study. While for estimating processing factor, the cardamom sample at 21 days after spraying of monocrotophos was used for pesticide estimation after subjecting it to processing. The processing part of cardamom included washing, curing (drying) under controlled temperature and polishing. The samples were cured at 50°C for 36 hrs and further for 3 hrs at 80°C. Polishing was done by rubbing the dried capsule in hot state against the steel mesh. Fresh and processed cardamom samples were analysed for the degradation of monocrotophos in the pesticide analytical laboratory, ICRI, Myladumpara.

The multiresidue estimation procedure recommended for fruits and vegetables (Anastassiades *et al.* 2003) was adapted for the analysis of pesticides residue of monocrotophos in the cardamom samples. Ten grams of homogenised cardamom for fresh sample analysis while for processed sample, 2 grams of ground sample in 10 mL water were used for analysis. The samples were taken in a 50 mL poly propylene centrifuge tube. 10 mL acetonitrile (Merck) was added to each sample. Magnesium sulphate anhydrous 4 g, Trisodium citrate dehydrate 1 g, Disodium hydrogen citrate sesquihydrate 0.5 g (Sigma Aldrich) and Sodium chloride 1 g (Merck), were added and shaken for 1 minute. The sample was centrifuged for 5 min at 3000 G-force. Supernatent solution (5 mL) was transferred to centrifuging tube. Magnesium Sulphate 150 mg mL^{-1} extract was added, shaken and centrifuged for 5 min. at 3000 G-force. Extracts are transferred into auto-sampler vials and used for the multiresidue determination by Gas Chromatography. The cardamom samples were analysed in duplicate for both pesticide residue analysis and estimation of processing factor.

Gas chromatography (Shimadzu model no. 2014, Japan) equipped with a Flame Photometric Detector (FPD) and capillary having 30 meter length and 0.25µm inner diameter was used. Nitrogen was the carrier gas at a flow rate of 1.5 mL min^{-1}. The injection port temperature was 250°C with split ratio of 10 and the detector temperature was 300°C. The column temperature was programmed from 200°C to 290°C. Two micro litre of the extract was injected and quantification of the insecticide was done by measuring the peak areas with the reference standard (Sigma-Aldrich) (Fig. 1).

To determine the rate of degradation of monocrotophos, first order rate equation $C = C_0 e^{-kt}$ was used. The half life ($t_{1/2}$) was determined using the equation $t_{1/2} = \ln 2/k$ and pre harvest interval (PHI) for processed cardamom to reach below MRL was calculated by using the equation:

$$PHI = \ln(C_0 \times PF/MRL) / k$$

Where, C=concentration in mg kg^{-1} at time t; C_0=initial concentration in mg kg^{-1}; t=time in days; $t_{1/2}$ =half life of decomposition in days; PF=Processing factor

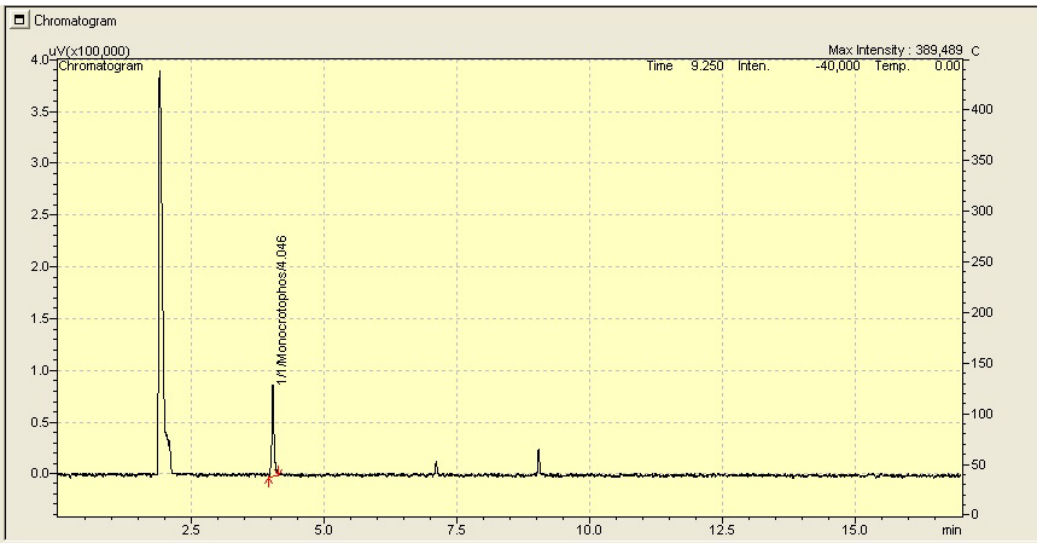

Fig. 1. Sample chromatogram of monocrotophos

Table 1. Kinetic parameters for the degradation of monocrotophos in cardamom under the field conditions

Rate equation	$C = 22.84e^{-0.14t}$
Correlation coefficient : R^2	0.95
Rate constant :k ($days^{-1}$)	0.14
Half-life: $t_{1/2}$ (days)	5.0

The processing factor (PF) was calculated as:

PF = [Residue in processed cardamom in mg kg^{-1} (dry weight basis)] / [Residue in fresh cardamom in mg kg^{-1} (fresh weight basis)]

The response of the detector for monocrotophos was linear in the range of 0.05-4.0 mg kg^{-1}. The equation of the best-fit curve was $y=2.208 \times 10^6X + 0.29$ (n=10) and the correlation coefficient (R^2) was 0.98. The control samples were fortified with monocrotophos 0.1,1.0 and 5.0 mg kg^{-1} and the percentage recovery of monocrotophos was found to be 95-110% with 10% coefficient of variation and method detection limit was 0.05 mg kg^{-1}.

The degradation of monocrotophos in cardamom capsules followed first-order kinetics at the rate constant (k) of 0.14 $days^{-1}$ and with a correlation coefficient (R^2) of 0.95. The data on degradation of monocrotophos in cardamom are presented in Tables 1 & 2 and in Fig. 2. The half-life of the insecticide was 5 days under the field conditions (Table 1).

Table 2. Degradation of monocrotophos in fresh cardamom samples

Days	Monocrotophos in cardamom capsules (mg kg^{-1})
1	16.7
3	13.2
5	10.2
7	6.7
9	7.0
12	5.9
14	5.7
16	3.5
18	2.7
20	1.0
22	0.56
25	0.26
27	0.45
30	0.28
33	0.17
36	0.12
39	0.15

Monocrotophos residue in cardamom before drying was 0.88 and 5.0 mg kg^{-1} respectively on fresh weight basis and when expressed on dry weight basis hypothetically. After curing,

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C : Concentration in mg kg^{-1} at time t
R^2: Correlation coefficient

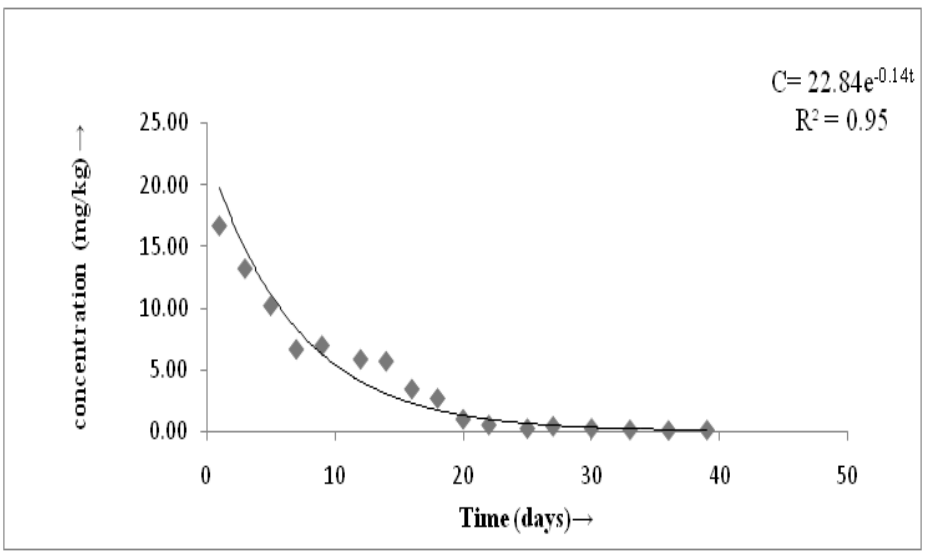

Fig. 2. Degradation of monocrotophos in cardamom

residue was 4.4 mg kg^{-1} and on polishing 3.1 mg kg^{-1} on dry weight basis (Table 3). There was a total of 37.6% of reduction of residue was observed in cardamom during processing. Out of which, 29.6% of reduction of residue was observed during the polishing and only 11.5% reduction on curing.The residue was found to be get magnified 3.5 times during processing due to the weight loss of the cardamom during drying. Hence processing factor was found to be 3.5. Application of chlorpyriphos at a concentration of 0.05% in cardamom followed by curing as per the farmers adopted practice and polishing resulted in 3.5 times more residues in cured product (George *et al.* 2013). The drying processes may result in higher concentrations of residues due to loss of moisture (Holland *et al.*1994).

MRL level prescribed by European Commission for monocrotphos is 0.05 mg kg^{-1} (EU Pesticides database 2014) for processed cardamom. We need to keep a pre harvest interval (PHI) of 53 days to reach EU MRL level for processed cardamom when monocrotophos was applied at a concentration of 0.072%.

Table 3. Effect of processing on residue of monocrotophos in cardamom

Stages	Residue (mg kg^{-1}): Dry matter basis
Before processing	5.0
Curing	4.4
Polishing	3.1

When monocrotophos was applied in cardamom at a concentration of 0.072%, half life was found to be 5 days under field conditions. To reach EU MRL level (0.05 mg kg^{-1}) for processed cardamom, keep a pre harvest interval (PHI) of 53 days in those regions where this chemcial is not banned like Tamil Nadu and Kartnaka. Reduction of monocrotophos was more while polishing by rubbing the dried cardamom capsule in hot state against the steel mesh than drying at 50 to 80°C during processing.

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