CHEMODYNAMICS OF CARBOFURAN IN CUCUMBER

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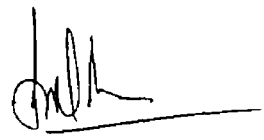
DECLARATION

I hereby declare that this thesis entitled Chemodynamics of Carbofuran in Cucumber is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award of any degree diploma associateship fellowship or other similar title of any other university or society



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Certified that this thesis entitled Chemodynamics of Carbofuran in Cucumber is a record of research work done independently by Shri ANIL ABRAHAM under my guidance and supervision that it has not previously formed the basis for the award of any degree fellowship or associateship to him

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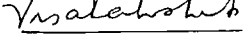

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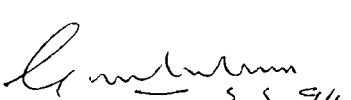

EXTERNAL EXAMINER

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INTRODUCTION

Vegetables have an important role in human nutrition According to ICMR an adult individual should consume 300g of vegetables per day for meeting the nutritional requirements But the average consumption is far below this level The major hurdle in achieving the targets in vegetable production is the heavy incidence of pests and diseases in field and store

Granular formulation of insecticides are widely used for pest control on a number of crops like vegetables rice maize sugarcane banana etc It generally affords protection to the crop from pests for 4-6 weeks after treatment (Agnihotrudu and Mithyantha 1978)

Among the granular formulations carbofuran is widely used by the vegetable growers because of its effectiveness in controlling the pests especially the fruit flies It is recommended and being used extensively for controlling a number of vegetable pests (Mathur et al 1974 Krishnaiah et al 1976) But the present Package of Practices Recommendations of KAU advocate the use of carbofuran only at seeding in vegetables for controlling various pests As against this the farmers are widely using the chemical even at the flowering stage of the crop Preliminary studies have shown that such treatments may cause insecticide residues as a

severe problem A recent study conducted by Rajendran and his co workers (1991) supported this fact Samples of bittergourd brinjal and cucumber collected from vegetable growers and local markets in Taliparamba and Panniyoor region showed high levels of carbofuran residues Residues of carbofuran were found to persist in cucumber fruits above the MRL of 0 2 ppm upto three weeks after application (Beevi et al 1991a) So to ensure safety to human beings waiting periods have to be fixed for each insecticide under various climatic conditions

The understanding of the behaviour of the chemical in the plant and the risk involved in using the insecticide at later stages of the crop will help to develop methods to minimise the residue hazards Detailed studies regarding the fate of carbofuran in cucumber plants have not been attempted so far

Here in the present study detailed investigations were taken up with the following objectives

1 To study the absorption and translocation of carbofuran in the plant system when applied in the soil at different growing stages viz sowing vining and flowering

2 To study the persistence and metabolism of carbofuran in leaves vines and fruits of cucumber when applied at different growth stages

3 To study the distribution of residues in the various portions of cucumber fruits

4 To study the degradation of residues in the fruits when stored for different durations

REVIEW OF LITERATURE

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REVIEW OF LITERATURE

Available literature on the uptake metabolism translocation and persistence of carbofuran in crop plants is reviewed hereunder

1 1 Uptake translocation and metabolism of carbofuran in crop plants

Dorough (1968) studied the metabolism of carbofuran in bean plants Hydrolysis oxidation and conjugation were observed as the three most important steps in the metabolic pathway Major metabolites detected in bean plant were 3 hydroxy carbofuran and carbofuran 7 hydroxy phenol

Metcalf and others (1968) studied the metabolism of carbofuran (Furadan) in plants (cotton) insects (Estigmene acrea) and mammals They found that carbofuran was metabolised by hydroxylation to 3 hydroxy carbofuran which was subsequently oxidised to 3 keto carbofuran The phenols were present either in the free state or as conjugates principally the glucosides in the various biological systems

Ashworth and Sheets (1970) studied the absorption and translocation of c^{14} labelled carbofuran in one month old tobacco plants It was readily absorbed from the nutrient solution and

was completly translocated to the leaves without accumulation in the root Autoradiography of the freeze dried plants indicated that accumulation was more in older leaves than in the region of terminal bud In the case of leaves labelled carbouran was not readily absorbed from the nutrient solution and even when it was absorbed it was not translocated from treated leaf to other parts of the plants

Kuhr (1970) reported that the metabolic fate of carbamate insecticide was very similar in plants and insects Hydrolysis of carbamate ester linkage was usually slow and the oxidation of the aromatic ring subsistuents and the carbamate N methyl group was of prime importance Hydroxlated metabolites were rapidly conjugated in vivo

Ashworth and Sheets (1972 a) reported that the carbofuran which had been absorbed in tobacco plants through the roots or through the petioles of isolated leaves was metabolised with a half life of about 4 days by progressive hydroxylation and oxidation to 3 keto carbofuran All these carbamates were hydrolysed to their corresponding phenols and were conjugagted as their respective glycosides 3-hydroxy carbofuran and its glycosides 3 hydroxy carbofuran and its glycosides were the major metabolites found in the carbofuran treated tobacco plants

lopically applied carbofuran in tobacco plants was more persistent due to the fact that it was not subjected to plant metabolism as a result of poor penetration into the cuticle (Ashworth and Sheets 1972 b)

Studies using Dalbulus maidis (De Long and Wole) to find out the toxicity of carbofuran in maize plants when used as granules in seed furrow at sowing showed that the toxicant was translocated to the upper portion of the plant the concentration was too low compared to that of lower parts (Bhirud and Pitre 1972)

Pree and Saunders (1974) observed that carbofuran phenol 3 keto carbofuran phenol and two unknown metabolites were present in mugho pine (Pinus mugho) in addition to 3-OH carbofuran An increase in 3 Keto Phenol in the treated plants was accompanied by decreased levels of 3 OH carbofuran

Huynh et al (1975) studied the metabolism of carbofuran in rice plants in sunlight and in laborotory conditions at different temperatures and light intensities Carbofuran phenol 3 OH carbofuran 3-Keto carbofuran and 7 unknown metabolites were deteced by thin layer chromatography Rapid degradation of the compound was noticed under sunlight or at high temperature and strong light intensities

Talekar et al (1977) observed that after soil treatment of labelled 14 C-carbofuran and 14 C phorate both the insecticides were readily translocated to the leaves of 2 weeks old seedling of both soybean and Mungbean Measurable but insignificant amount of radio carbon were present in the seeds of plants grown in treated soil

Mohamed Ali (1978) reported that the translocation and persistence of carbofuran was much greater in the paddy leaves than in stems and as a result there was increased mortality among the hoppers when fed on the leaves than on the stems

Rouchaud et al (1990) observed that carbofuran applied to soils of cauliflower brussels sprout and sugarbeet (at sowing) was absorbed more intensively and for longer periods In the foliage carbofuran was metabolised rapidly to 3 OH carbofuran

Gaybhiye et al (1991) studied the fate of 14 c carbofuran in model ecosystem Carbofuran applied directly to maize plant leaves and in nutrient solution was studied Uptake from nutrient solution was rapid with 39 3% of the applied activity absorbed by plants within 3 days The concentration of the insecticide in shoots was less than in roots and about 45-60% of the residues constituted as water soluble metabolites and their conjugates

1 2 Persistence of carbofuran in different crops

1 2 1 Rice

Studies on the control of grassy stund disease and its vector Nilaparvata lugens (Stall) conducted in IRRI Manila showed that carbofuran applied to rice seedlings did not persist effectively so as to cause significant reduction in disease incidence (Anon 1969)

Application of carbofuran 3G at the rate of 0 2 Kg ai/ha 10 days after sowing (nursery) proved to be effective in controlling the stem borer incidence in the transplated crop upto 20 days (Anon 1973)

Rao and Das (1977) studied the persistence of carbofuran in paddy when planted with seedlings the roots of which was dipped in mud slurries containing 0 1% carbofuran They found that 70 and 50% of last instar nymphs of Nilaparvata lugens were dead when they are exposed on plants for 24 hrs on the 11th and 20th day after treatment respectively

Rajukannu et al (1977) estimated the residues of carbofuran and phorate in hulled grains bran and straw following soil application @ 1 25 kg ai/ha in two split doses under flooded conditions in paddy fields Granules were applied along the rows

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Residues were present in bran also which were estimated as 0 11 ppm and 0 18 ppm for 0 75 and 1 kg ai/ha respectively

of paddy plants with 5 cm water No residue could be detected in bran but residues of 0 057 ppm and 0 192 ppm were present in hulled grains and straw respectively

Saivaraj and Venugopal (1977) estimated carbofuran residues present in paddy husk and straw following two doses viz 0 75 kg ai/ha and 1 kg ai/ha applied twice and thrice at 20 days intervals commencing from 15 or 20 days after transplantation Residues of carbofuran at 0 75 kg ai/ha were 0 04 ppm in grains for two rounds and 0 1 ppm for three rounds At 1 kg ai/ha it was 0 04 ppm and 0 17 ppm for two and three rounds respectively Residues were present in bran also which were estimated as 0 11 ppm and 0 18 ppm for 0 75 and 1 kg ai/ha respectively

Mohamed Ali (1978) studied the persistence of carbofuran residues in straw and in grain of rice plants treated at different stages after transplantation and found that the application of the granule at 60 days after transplantation alone left residues in the straw

Sundararaj (1985) studied the persistence of carbofuran in paddy when applied twice in nursery and once in mainfield (20 DAP) for controlling of Orseolia Oryzae, Cnaphalocrocis medinalis and Hydrellia sp and found that residues in straw and grain ranged from 0 041 to 0 092 ppm which was far below the tolerance level of 0 2 ppm

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Carbofuran was detected in all the paddy fractions viz paddy grain rice bran husk and straw at harvest after two applications @ 1 & 2 kg ai/ha at 20 and 45 days after planting Maximum residues were recorded in straw (0 017 and 0 057 mg/kg for 1 & 2 kg ai/ha respectively) followed by rice (0 015 and 0 035 mg/kg) paddy grain (0 015 and 0 027 mg/kg) Husk (0 010 and 0 026 mg/kg) and bran (0 009 and 0 021 mg/kg respectively) However the carbofuran residues at harvest recorded below the tolerance limit of 0 2 mg/kg in water and paddy fraction (Anon 1990 a)

Studies carried out at Haryana Agricultural University Hisar revealed that carbofuran when applied at the rate of 1 0 Kgai/ha for rice plants at 60 days after transplanting was found to be safe whereas the application at 80 days after transplanting and 60 + 80 days after transplanting resulted in residues in grain above the MRL value (Anon 1990 b)

A study conducted at Rajendra Agricultural University Bihar showed that carbofuran residues in rice grains and husk after granular application at the time of transplanting was below the MRL value (0 2 mg/kg) for both the doses of 0 75 and 1 5 kg ai/ha (Anon 1990C)

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1 2 2 Maize

Caro et al (1973) reported that upto 0 14% of applied carbofuran was accumulated in maize a major portion being 3 OH carbofuran and it decreased sharply before harvest Residues were mostly in leaves and the carbamate content in the yield was below the tolerance limit

Marwaha and Sarup (1978) studied the level of carbofuran in the stem and in the leaves of maize plants at various development stages and in grains at harvest following a side dress application of granules at the rate of 1 875 kg ai/ha to the soil around the roots when the crop was 15 day old or when applied twice at 15 and 30 days after sowing Residue concentration of carbofuran in plants collected at 1 5 10 15 25 and 35 days after treatment were 32 0 38 4 26 4 9 10 4 26 and 1 32 ppm respectively and those in samples collected at 25 and 35 days after sowing were 16 0 and 9 1 ppm respectively Residues in stems leaves and grain at harvest were non detectable

Sahu and Agnihotri (1983) reported that a study carried out in Delhi in the kharif season (1975 76) showed that carbofuran applied as side dressing at 0 6kg ai/ha to the maize crop persisted in the soil for about 30 days in the first year and for 45 days in the second year The corresponding residues in the leaves stems and whole plants had fallen below the tolerance

level within 45 days The residues were concentrated mainly on the leaves and they were not detectable in the grain samples taken at green cob stage or at harvest

Rajukkannu et al (1990) reported that application of carbofuran to maize crop at 15 & 25 days after sowing controlled the root lesion nematodes Pratylenchus zea and Helicotylenchus incisus and the residues did not persist in the grain at harvest (105 days after treatment) However when carbofuran was applied at the time of sowing and at 15 20 and 25 days after sowing the residues in grains were 0 06 and 0 084 ppm respectively The values were below the MRL

1 2 3 Sorghum

Gupta and Dewan (1974) analysed the toxic residues of carbofuran n sorghum when applied at the dose of 0 4 to 1 33 kg ai/ha for controlling sorghum shoot fly The application of the insecticide was found to be safe as it dissipated fast and no build up of toxic residues of either parent compound or its metabolites was noticed in the harvested produce Whorl application of carbofuran in sorghum at 22 5 kg /ha in three split doses at 20 30 and 40 days after sowing resulted in a residue concentration of 0 11 ppm in the straw

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Srivastava (1976) reported that carbofuran was degraded to non detectable level in sorghum plants and in soils in 60 to 90 days Large amounts of insecticides were found in leaves and stems at the time of harvest and sorghum grains were also found to contain residues but below the tolerance limits

Srivastava and Jotwani (1977) observed that carbofuran applied as Furadan 3G at the rate of 2 3 and 4g/metre row of sorghum crop left an initial residue level of 5 6 9 and 10 8 ppm respectively which was reduced by 58 52% 75% and 61 75% respectively within 7 days after treatment After 30 days the extent of reduction in the level of residues was almost similar in all treatments

Ramamoorthy et al (1991) reported that following soil application of carbofuran at 1 50 or 3 0 g ai/m of row before sowing sorghum that the freshly harvested seeds contained 0 1482-0 224 ppm

1 2 4 Pulses

Bhattacharjee and his co workers (1975) have analysed the leaves and pods of soybean at different stages of growth following soil application of 3% granules of carbofuran No parent material or its 3 OH metabolite could be detected in the plant parts after 65 days during kharif season and after 85 days during spring

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Handa et al (1977) studied the residue levels in soybean leaves and pods resulting from insecticide schedules involving soil application of 3% granules of carbofuran at 5 5 g employed for the control of Ophiomyia phaseolus, Melanagromyza phaseoli, Bemesia tabaci and Myllocerous sp There were excessive residues on leaves and pods at 65 days However the residue levels were safe after 80 days and were undetectable at harvest

Dikhsit et al (1980) studied the residues of carbofuran in soybean crop and found no residues in seeds or straw or husks of the plant at harvest

Nanda kumar (1981) studied the persistence of residues of granular insecticides in cowpea pods He reported that the insecticides namely disulfoton carbofuran and phorate left residues in the pods and the residues persisted in the plants for a period of 45 days after application and the level of carbofuran residues in harvested pods ranged from 0 066 to 0 127 ppm

Faleiro et al (1985) studied the dissipation of carbofuran and carbaryl in cowpea Granular carbofuran was applied at 0 5 kg ai/ha at sowing and residues were estimated in soil for 35 days during kharif Residues were detected in cowpea plant for 35 days after sowing in kharif and 28 days after sowing in summer irrespective of the cropping pattern The residue half life and

safety interval for carbofuran were 8 96 and 54 44 days respectively

The residues of carbofuran in black gram grown as sole crop or intercropped with other plants and in soils were studied in Delhi in 1982 following the application of the insecticide to plots at the dose of 0 5 kg ai/ha In summer there was no detectable residues in soil under blackgram In plant samples there was no detectable residues left 30 days except in black gram grown as sole crop the residue was 0 08 ppm (Dhuri et al 1989)

A study was conducted at Jaipur on the persistence of carbofuran in chickpea and associated weeds At the lower dose (1 98 kg ai/ha) the residues persisted upto 90 days in associated weed plants as well as in the green pods of chickpea However the grains at harvest did not show any carbofuran residues (Anon 1990d)

Habeebullah & Balasubramanian (1991) studied the dissipation and persistence of certain insecticides on cowpea pods (Var C 152) when applied at the time of sowing The terminal residues of carbofuran was 0 2 ppm and that of phorae was 0 3 ppm and these levels were high considering their tolerance limits The terminal residues of carbofuran was 0 2 ppm which is the same amount prescribed as tolerance limit

1 2 5 Fruit Crops

Archer et al (1977) studied the fate of carbofuran and its metabolites on strawberries Day Neutral Troga and Tufts sprayed once with carbofuran (Furadan 4 flowable) at the rates of 4 and 8 oz ai/acre during fruit maturation The berries and leaves were sampled and the residues of carbofuran and its metabolites were determined The combined residues on berries never exceeded the tolerance level of 0 5 ppm nor did the carbamate fraction exceed 0 2 ppm on 6th day after application In some instances the amount of the metabolites 3 7 diol and 3 oxo carbofuran increased until 7 days after application and then decreased in amounts to harvest Reduction of residues probably resulted from dilution by plant growth and volatilisation from plant tissue surfaces

Vasconellos et al (1983) reported that in course of tests in oranges Citrus Sinensis in Rio de Janeiro to control insect pests by soil application of granular preparation containing 5% carbofuran at 400 300 200 and 100g/tree respectively Orange fruits analysed at 90 days after treatment contained carbofuran at 0 13 0 12 0 10 and less than 0 05 ppm respectively

The persistence of carbofuran was studied in grapes at Haryana Agricultural University The results indicated that from lower

treatment (4 0 kg ai/ha) the residues varied from non detectable to 0 043 ppm in grape berries whereas the corresponding figures from higher dose (6 0 kg ai/ha) varied from nondetectable to 0 096 ppm (Anon 1990b)

1 2 6 Sweet potato and groundnut

Rajukkannu et al (1976) reported that soil application of carbofuran granules at 1kg ai/ha at the time of tuber formation for the control of sweet potato weevil Cylas formicarius resulted in residues upto 0 105 ppm in tubers which was below the FDA tolerance level

Balwinder Singh and Kalra (1992) studied the persistence of carbofuran in groundnut crop The results indicated that the combined residues of carbofuran and its metabolites reached below the detectable level in groundnut plants after 60 days of sowing Total carbofuran residues remained below MRL (0 1mg/kg) in groundnut kernals at harvest

1 2 7 Vegetables

Finlayson et al (1976) reported that in carrot the carbofuran residues were detected in higher quantities in the peel than in the pulp The accumulation of residues were more in the top

portion than in the lower portion of carrot Residue levels increased with higher rates and number of application

Mithyantha et al (1977) analysed the brinjal plants for its carbofuran residues harvested at 7 21 37 52 & 75 days after treatment with 1 3 and 10g/plant (corresponding to 0 26 0 78 and 2 61 kg ai/acre) On the 7th day the residues varied between 0 088 to 0 171 ppm and it decreased to 0 027 ppm after 75 days It was found that boiling the fruit in salt water removed large portions of the residue

Krishnamoorthy et al (1978) reported that application of carbofuran at 0 5 kg ai/ha at sowing/planting of peas okra and sweet potato were safe to avoid residues in fruits

Carbofuran and aldicarb were applied to the soil in band treatment at 1 25 kg toxicant/ha at the time of fruit set in chillies Chillies were harvested at fortnightly intervals until the fruits remaining on the plant were ripe and red The insecticides almost cleared the crop pests within 8 days but left residues so high as to make chillies harvested upto 45 days after application unfit for human consumption After 60 days the residues dropped to very low or undetectable levels These results indicated that only ripe red chillies and not green ones could be harvested after soil treatment with carbofuran or aldicarb granules (Rajukannu et al 1978))

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Following granular application of carbofuran to the soil in radish plots at 0 5 and 1 0 kg ai/ha at transplanting to 45 days old crop carbofuran residues degraded to safe levels in the edible part of the plant within 45 days However the green pods were found to contain toxic levels of carbofuran residues when harvested at 70 days after treatment (Awasthi and Anand 1987)

A study was conducted to assess the contamination of bitter gourd fruits due to the applicatioi of carbofuran at the flowering stage The results showed that when carbofuran was applied at 0 5 kg ai/ha the residues in mature fruits harvested at 1 3 and 7 days after treatment were 5 6 and 5 times above the MRL and when applied at 1 0 kg ai/ha it was 7 7 and 6 times respectively The residues reached below the MRL of 0 2 ppm in 21 and 22 days when applied at 0 5 and 1 0 kg ai/ha respectively The effect of cooking reduced the residue content by 33 34% However the residues in mature fruits were not detectable when the crop was treated with carbofuran at the time of sowing (Beevi et al 1991b)

Beevi et al (1991a) reported that the residues of carbofuran were found to persist in cucumber fruits above the MRL of 0 2 ppm upto 3 weeks after the application No detectable residues were present when treated at the time of sowing but when applied at the flowering stage maximum residues were seen on the third day

after treatment the values being 2 88 and 3 38 mg/kg respectively for 0 5 and 1 5 kg ai/ha which reached below the maximum residue limit in 23 days

Misra and Dikshit (1991) reported that when carbofuran at 1 0 and 1 5 kg ai/ha was applied to the soil of potato crop the residues in unprocessed potatoes persisted above the tolerance limit of 0 5 ppm for up to 118 days after planting The residues of insecticide in processed potatoes or water obtained after cooking were below the tolerance limit

In a very recent survey conducted by Rajendan and his co workers (1991) the samples of bittergourd brinjal and cucumber collected from vegetable growers and local markets in Taliparamba and Panniyoor region showed higher levels of carbofuran residues

1 2 8 Betel Vine

Carbofuran 3G when applied to one year old betel vine (Piper betle) at 0 5 and 1 0 kg ai/ha residues were non detectable after 41 days and half life values for 0 5 and 1 0 kg ai/ha were 6 and 7 days respectively The time of residues to reach safe for human use was 12 and 15 days (Rajukannu et al 1988)

Carbofuran when applied at 1 and 2 kg ai/ha in single application on first year betel vine crop the maximum residues recorded were

1 157 and 1 587 mg/kg respectively at 10 days after application which got dissipated to 99 96% in 60 days after application The time required to dissipate the chemical to below the tolerance limit of 0 2 mg kg^{-1} was 33 09 and 40 78 days respectively (Anon 1990a)

A study conducted at Jorhat in betel vine crop showed that the residue levels on the leaves of betel vine were 0 608 0 221 0 073 0 045 and 0 002 ppm at 20 30 40 50 and 60 days respectively after application of the insecticide at 1 kg ai/ha In case of 2 kg ai/ha the residues were found to be 1 006 0 031 0 184 0 121 and 0 027 ppm at 20 30 40 50 and 60 days respectively (Anon 1990e)

1 2 9 Other Crops

In coastal bermuda grass the residues of carbofuran and its substituted furanol dissipated to non detectable level in 14 days when applied at 1 lb/acre However the residues of carbofuran were found to be relatively stable in coastal bermuda grass silage stored for 30 days (Levek et al 1968)

Shaw et al (1969) estimated the residues of carbofuran and 3 OH carbofuran in alfalfa following spray applications of 0 5 and 1 lb toxicant per acre After 21 days of the foliar sprays to the

first crop lucerne the residues of carbofuran and 3 OH carbofuran were nondetectable and 0 55 ppm for the first dose whereas it was 0 2 ppm and 1 6 ppm for the second dose The residues of carbofuran and 3 OH carbofuran for 0 5 lb/acre were 0 2 ppm and 0 1 ppm and for 1 lb/acre corresponding values were 0 2 ppm and 4 4 ppm respectively

Fahey et al (1970) reported that trials carried out using emulsion sprays of carbofuran 0 516 and 1 lb toxicant in 20 US gal/acre resulted in residue levels of 48 ppm and 136 ppm respectively on green lucerne on the date of treatment and the residues were less than 0 2 ppm after 14 days Application of carbofuran granules at 0 66 lb/acre in 12 band or at 0 5 lb/acre broadcast before planting followed by 3 spray application at the rate of 1 lb/acre in 100 gal of water at two weeks interval resulted in residue concentration of carbofuran up to 0 2 ppm in treated plots and 0 1 ppm in untreated plots

Pree and Saunders (1974) reported that the analysis of foliage and buds from mugho pine (Pinus mugho) grown in carbofuran treated soils showed that application of 2g/tree produced a peak concentration of 283ppm and 1g/tree and 0 4g/tree produced 106 ppm and 36 ppm respectively The presence of toxicant can be detected within one week and concentration increased for 60 90 days before declining Active residues persisted for at least 2 years

Archer and Engebreston (1988) investigated the residues of carbofuran and its metabolites in green and dry hops by gas chromatography Carbofuran was applied at 1 12 kg ai/ha for the control of Otiorhycnhus Sulcatus and Otiorhycnhus ovatus In all the cases and green and treated hop cones also had residues of less than 0 05 ppm Dry treated hop cones contained <0 05 ppm of all chemicals except 3 keto 7 phenol (0 12 ppm) and 3 7 diol (0 07 ppm) The residues were below the tolerance limit

MATERIALS AND METHODS

MATERIALS AND METHODS

2 1 Lay out ard Plantıng

An experıment was laıd out ın the vegetable crchard attached to the Instructıonal Farm College of Agrıculture Vellayanı, durıng - August 1992 to study the pattern of absorptıon, translocatıon metabolısm and persıstence of carbofuran ın cuccumber The experıment was laıd out ın 3 x 2+1 factorıal desıgn usıng the varıety 'Mudıcode local' Carbofuran as furadan 3G was applıed at two doses, sevent days after germınatıon at 0 5 and 1 5Kg aı/ha at three tımes vız sowıng,vınıng (30 DAP) and flowerıng stage (60 DAP) of the crop There were three plants ın each pıt and twelve such pıts where there ın each treatment Lach treatment was replıcated thrıce and untreated plots served as control To mınımıse the chances of contamınatıon among plots ın the fıeld experıment, strong bunds and buffer plots were provıded All the cultural operatıons excludıng the plant protectıon measurcs were followed as per package of Practıces Recommendatıons of KAU (1989) The weather condıtıons prevaılıng durıng the experımental perıod and the physıcal and chemıcal propertıes of the soıl are furnıshed below

2 2 Weather elements

Average raınfall -- - 58 mm

Maxımum Temperature -- - 30° C

Minimum temperature 22 °C

2 3 Physical properties

Soil type	Lateritic red loam
Course sand	46%
Fine sand	22%
Silt	4 8%
Clay	25%

2 4 Chemical properties

pH	4 8
Organic matter	1 56%
Total Soluble salts (E C)	Trace
Cation exchange capacity	6 cmol(p+)kg^{-1}

2 5 Application of the insecticide

Furadan 3G formulation of Carbofuran supplied by M/s Rallis India Ltd Bombay was used The insecticide granule required for each plot was weighed out at each time mixed with an equal quantity of dry sand and the insecticide sand mixture was applied uniformly in the plots by broadcasting

2 6 Collection of Samples

Samples of leaves vines and fruits (when available) were collected on 1 3 7 14 21 and 28th day after application of the insecticide from the treated and the control plots Samples were collected in paper bags and immediately brought to the laboratory for processing The fruit parts like peel pulp placenta and inner flesh were subjected to analysis separately to estimate the residues in these portions of the fruit In order to study the distribution of residues in the basal middle and distal portions of the fruit these portions were also analysed separately

The degradation of carbofuran in fruits stored under refrigeration for different durations (0 1 4 5 7 & 10 days) was also studied by estimating the residues in the samples stored for the above durations

2 7 Analysis of the sample

2 7 1 Extraction

Twenty five gram each of the finely chopped material (leaf vine & fruit) was taken in a 500ml conical flask Three hundred ml of 0 25N HCl was added and the flask was connected to a leibig condenser and refluxed the mixture on a heating mantle for

one hour with occasional swirling of the flask by hand At the expiry of this period the condenser was disconnected and the hot sample was filtered through glass wool in to a 1000ml erlenmeyer flask The condenser flask and the cotton wool were washed with an additional 150ml of hot 0 25 N HCl The filtrate and the washings were pooled and allowed to cool for one hour

The HCl extract was then transferred to a one litre separatory funnel About 0 25g of sodium lauryl sulphate was added and mixed well This aqueous phase was extracted thrice each with 50ml portions of redistilled dichloromethane The lower dichloromethane extract was drawn out and was passed through a layer of anhydrous sodium sulphate kept over a funnel with a glass wool pad in order to remove any water droplets present The dichloromethane extracts were combined and transferred to a Kuderna Danish evaporative concentrator The extract was concentrated on a water bath to about 10ml

2 7 2 Clean up

A chromatographic column was prepared in the following order in distinct layers a layer of glasswool 1g of anhydrous sodium sulphate 10g activated alumina 10g of silicagel and 2g of anhydrous sodium sulphate The column was washed with 50ml of

methylene chloride without allowing the solvent to fall below the upper layer of the absorbent packing The concentrated extract was slowly poured into the column followed by three washings with 10ml portions of methylene chloride When the last liquid was percolated into the column 100ml of diethyl ether and dichloromethane (2 1) was added and the elute was collected at the rate of 2ml per minute Three drops of propylene glycol was added and the eluate was evaporated to almost dryness in Kuderna Danish evaporative concentrator

2 7 3 Estimation by gas chromatographic method

Principle The Carbofuran residue in the extract after clean up was hydrolised under alkaline conditions to its phenol and was derivatised to its 2 4 dinitro benzene The derivative was extracted in n hexane and estimated by gas chromatograph using an Electron capture detector(ECD)

2 7 4 Reagents

Phosphate buffer

Phosphate buffer of pH 11 was prepared by dissolving 25g of Na_2HPO_4 in 2480 ml of distilled water and adding 20ml of 1M NaoH solution to the above with thorough mixing

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Reactant

The reactant was prepared by dissolving 1 0g of 1 Fluoro 2 4 dinitro benzene in 100 ml of acetone

2 7 5 Derivatization

The residue obtained in the cleanup was dissolved in 3 ml of the reactant solution and transferred quantitatively to stoppered 25mmx190mm test tubes Fifteen ml of the buffer solution was added mixed well and kept in a water bath maintained at 50 °C for 30 minutes The mixture was cooled and transferred to a 125ml separating funnel The mixture was extracted thrice with 25ml portions of n hexane and the hexane extracts were pooled

2 8 Gas Chromatrographic conditions

A Gas Chromatograph Chemito model 3865 equipped with an electron capture detector was operated under the following parameters

Column glass 60cm long and 4mm id packed with 5% OV 210

Column oven temperature 230 °C

Injection port temperature 245 °C

Detector temperature 280 °C

Gas flow rate Nitrogen 60ml/mts

Recorder chart speed 1cm/min

2 9 Estimation

Two ul of the hexane extract of the derivative was injected into the gas chromatograph The peak for carbofuran and its metabolites were identified based on the retention time and the area was measured The contents were determined by comparing the response for a known standard of similar concentration

Calculation

Residues (mg/kg) in terms of ug

$$\frac{\text{Peak height of the sample}}{\text{Peak height of standard}} \times \frac{\text{Quantity of standard injected (ng)}}{\text{Volume of the sample injec}} \times \frac{\text{Final volume of the sample (ml)}}{\text{Weight of the sample (g)}} \times \frac{100}{\text{Percent mean recovery}}$$

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Recovery

Twenty five gram each of the chopped leaves vines and fruits were fortified with 40 60 & 80 ul each of pure carbofuran 3 OH carbofuran and 3 keto carbofuran and kept over night The samples were then blended and extracted The insecticides in the extracts were estimated following the same method used as in the case of soil samples The average percent recoveries from plant samples fortified with 3 hydroxy carbofuran and 3 ketocarbofuran fortified with 1 0 mg/kg were 84 81 and 86 percent for carbofuran 3 hydroxy carbofuran and 3 keto carbofuran respectively The limit of detection was 0 5mg/kg for carbofuran 3 hydroxy carbofuran and 3 keto carbofuran

RESULTS

RESULTS

3.1 Absorption and Metabolism of carbofuran in the leaves of cucumber plants when applied at sowing

The nature and level of carbofuran residues found in the leaves of cucumber when applied at 0.5 and 1.5 kg ai/ha at sowing are given in Table -1. The results indicated that the absorption and metabolism of carbofuran was initiated on the first day after treatment as evidenced by the presence of the metabolites Viz 3 OH carbofuran and 3 keto carbofuran along with the parent compound pure carbofuran. The parent compound was present in the leaves upto 21 days after treatment (DAT) when applied at 0.5 kg ai/ha at one week after sowing. But when applied at 1.5 kg ai/ha the presence was noticed upto 28 DAT. Maximum residues of pure carbofuran was seen on the first day after application the value being 0.194 mg/kg for the lower dose which got reduced to 0.017 mg/kg by the 21st day after treatment. The plant sample collected at 28 DAT did not show the presence of any residues of carbofuran. When applied at 1.5 kg ai/ha the initial level of pure carbofuran was 0.144 mg/kg and it was reduced to 0.022 mg/kg by the 28th day after treatment.

Table 1 Residues of carbofuran and its metabolites in the leaves of cucumber plants treated in the field at sowing

Days after treatment	mean level of residues(mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg ai / ha		
1	0 194 (+0 009)	0 266 (±0 14)	0 152 (+0 020)	0 611 (+0 055)
3	0 144 (+0 013)	0 428 (+(023)	0 423 (+0 013)	0 995 (+0 019)
7	0 138 (±0 015)	0 170 (+0 020)	0 152 (+0 015)	0 460 (+0 010)
14	0 114 (+0 013)	0 152 (+0 009)	0 120 (±0 008)	0 384 (±0 021)
21	0 017 (+0 007)	0 115 (+(014)	0 112 (±0 011)	0 244 (±0 009)
28	ND	0 061 (+0 013)	ND	0 061 (+0 021)
		1 5 kg ai / ha		
1	0 144 (+0 008)	0 264 (+0)1( )	0 223 (+0 013)	0 629 (±0 007)
3	0 117 (+0 009)	0 694 (+(22)	0 438 (+0 020)	1 248 (+0 016)
7	0 104 (+0 008)	0 393 (+))2 I)	0 307 (+0 019)	0 804 (+0 040)
14	0 026 (+0 010)	0 219 (+0) I)	0 175 (+0 017)	0 420 (+0 011)
21	0 023 (+0 007)	0 188 (+ 00)	0 164 (+0 009)	0 375 (±0 008)
28	0 022 (+0 012)	0 108 (+0 12)	ND	0 130 (+0 012)

ND Non Detectable

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When the crop was treated at 0 5 kg ai/ha the resıdues of 3 OH carbofuran found ın the leaves on the fırst day after applıcatıon was 0 266 mg/kg whıch reached the maxımum of 0 428 mg/kg on the thırd day and gradually reduced to 0 061 mg/kg by the 28th day after treatment When applıed at 1 5 kg aı/ha the ınıtıal level of 0 264 mg/kg got ıncreased to 0 694 mg/kg on the thırd day and then gradually decreased to 0 108 mg/kg on the 28th day after applıcatıon

As ın the case of 3 OH carbofuran the level of 3 keto carbofuran ın the leaves showed an ıncreasıng trend reachıng the maxımum on the 3rd day after treatment for both the doses The correspondıng levels were 0 423 & 0 438 mg/kg for the lower and hıgher dose of 0 5 & 1 5 kg aı/ha respectıvely From the above values the resıdues of 3 keto carbofuran decreased drastıcally below the detectable level by the 28th day after treatment for both the doses

Consıderıng the content of total carbofuran resıdues ın the leaves ıt was observed that maxımum concentratıon of carbofuran resıdues accumulated ın the leaves on the 3rd day after treatment the values beıng 0 995 and 1 248 mg/kg for the doses of 0 5 and 1 5 kg aı/ha respectıvely On the 28th day after

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treatment the total carbofuran fraction in the leaves was accounted by 3 OH carbofuran alone when applied at 0 5 kg ai/ ha while at the application rate of 1 5 kg ai/ ha this was accounted by both pure and 3 oH forms of carbofuran

3 2 Metabolism of carbofuran in the leaves of cucumber plants when applied at the vining stage of the crop

The data presented in Table 2 show the residues of carbofuran present in the leaves of cucumber when applied at 0 5 and 1 5 kg ai/ha at the vining stage of the crop The presence of metabolites viz 3 OH carbofuran and 3 keto carbofuran along with the parent compound were detected in the leaves collected on the very next day of treatment

The maximum concentration of pure carbofuran was observed in the leaves on the first day after treatment for both the doses of 0 5 and 1 5 kg ai/ha The initial levels of pure carbofuran observed in plants treated at 0 5 and 1 5 kg ai/ha were 0 166 and 0 314 mg/kg respectively These values decreased considerably to 0 038 and 0 053 mg/kg respectively by the 21st day after application The plant samples collected at 28 DAT did not show the presence of parent compound at both the doses tested

Table 2 **Residues of carbofuran and its metabolites in the leaves of cucumber plants treated in the field at the vining stage of the crop**

Days after treatment	mean level of residues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg ai / ha		
1	0 166 (+0 022)	0 288 (+0 010)	0 187 (+0 023)	0 582 (±0 050)
3	0 145 (+0 016)	0 476 (±0 040)	0 269 (+0 033)	0 890 (±0 030)
7	0 118 (+0 007)	0 280 (+0 020)	0 194 (+0 020)	0 594 (+0 007)
14	0 056 (+0 020)	0 131 (+0 020)	0 112 (+0 010)	0 299 (±0 020)
21	0 038 (+0 009)	0 059 (+0 010)	0 046 (+0 020)	0 143 (+0 030)
28	ND	0 029 (+0 020)	ND	0 029 (+0 020)
		1 5 kg ai / ha		
1	0 314 (+0 022)	0 504 (±0 024)	0 404 (+0 032)	1 223 (+0 013)
3	0 300 (±0 027)	1 625 (+0 093)	0 716 (+0 039)	2 641 (+0 153)
7	0 144 (+0 016)	0 631 (+0 047)	0 424 (+0 028)	1 198 (±0 010)
14	0 094 (+0 015)	0 342 (+0 031)	0 257 (+0 036)	0 693 (+0 040)
21	0 053 (+0 014)	0 157 (+0 034)	0 124 (+0 022)	0 335 (±0 060)
28	ND	0 082 (+0 023)	0 048 (+0 023)	0 129 (+0 028)

ND Non Detectable

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In the case of 3 OH carbofuran the residues in the leaves on the first day after application was 0 288 mg/kg which reached the maximum of 0 476 mg/kg on the third day and gradually decreased to 0 029 mg/kg by the 28th day when applied at 0 5 kg ai/ha A similar trend was noticed when the application was done at 1 5 kg ai/ ha the peak value being 1 625 mg/kg on the third day which got reduced to 0 082 mg/kg on the 28th day

As against the parent compound the level of 3 keto carbofuran showed an increasing trend reaching the maximum on the 3rd day after treatment for both the doses The residues reached to non detectable level by 28th day after treatment for the lower dose while upto 0 048 mg/kg was retained in plants treated with the higher dose The levels of 3 keto carbofuran observed in the leaves collected from plants treated with the lower dose on 7th 14th and 21st day were 0 194 0 112 and 0 046 mg/kg respectively The corresponding levels observed for the higher dose of application were 0 424 0 257 and 0 124 mg/kg respectively

The initial level of total carbofuran was 0 582 and 1 223 mg/kg when applied at 0 5 and 1 5 kg ai/ha respectively The corresponding values on the 3rd day were 0 890 and 2 641 mg/kg

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Approximately 1 5 times increase over the initial level was noticed on the 3rd day after treatment when applied at 0 5 kg ai/ ha while the increase was 2 2 times over the initial concentration when applied at 1 5 kg ai/ha By the 28th day the residue level has come down reached to 0 029 and 0 129 mg/kg for the lower and higher doses respectively

3 3 Metabolism of carbofuran in the leaves of cucumber plants when applied at the flowering stage of the crop.

The nature and extent of carbofuran residues found in the leaves of cucumber plants when applied with carbofuran at 0 5 and 1 5 kg ai/ha at the flowering stage of the crop is presented in Table 3 As in the case of treatments at sowing and vining stages of the crop the presence of 3 OH carbofuran and 3 keto carbofuran along with the parent compound was detected in the leaf samples collected on the first day after treatment itself

As in the case of other stages the level of pure carbofuran was maximum on the first day after treatment at the lower and higher doses The values were 0 102 and 0 466 mg/kg for the lower and higher dose respectively By the 21st day the residues increased to levels of 0 06 and 0 043 mg/kg for 0 5 and 1 5 kg ai/ ha respectively When applied at 0 5kg ai/ha the residues reached

Table 3 Residues of carbofuran and its metabolites in the leaves of cucumber plants treated in the field at the flowering stage of the crop

Days after treatment	mean level of res dues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg ai / ha		
1	0 102 (+0 038)	0 237 (+ 073)	0 101 (+0 055)	0 441 (+0 008)
3	0 072 (+0 024)	0 293 (+0 84)	0 129 (+0 096)	0 494 (+0 027)
7	0 068 (+0 022)	0 226 (+0 55)	0 115 (+ 042)	0 408 (+ 011)
14	0 064 (+0 017)	0 125 (+ 3( )	0 071 (+0 010)	0 261 (+0 017)
21	0 06 (+0 01)	0 027 (+ 11)	0 061 (+0 006)	0 148 (+0 021)
28	ND	0 027 (012)	ND	0 027 (+0 012)
		1 5 kg ai / ha		
1	0 466 (+ 125)	0 130 (+ 58)	0 239 (+0 141)	0 835 (+ 038)
3	0 183 (+ 051)	0 330 ± 15)	0 287 (0005)	0 934 (+0 003)
7	0 154 (+ 048)	0 320 (± 88)	0 318 (0 152)	0 793 (+ 051)
14	0 071 (+0 020)	0 164 (+ 5)	0 247 (+ 059)	0 483 (+ 2( )
21	0 043 (+0 015)	0 089 ± 1)	0 098 (+0 018)	0 231 (+0 033)
28	0 028 (+0 009)	0 039 (± 014)	ND	0 067 (+0) 3)

ND Non Detectable

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to non detectable levels on the 28th DAT while in the higher dose carbofuran persisted even upto 28 days after application

The initial concentration of 3 OH carbofuran was 0 237 and 0 130 mg/kg for the lower and higher dose respectively The peak value was attained on the third day after treatment for both the doses the values being 0 293 and 0 390 mg/kg respectively The presence of 3 OH carbofuran was detected in the leaves upto 28 DAT for both the doses and the observed values were 0 027 mg/kg for the lower dose and 0 039 mg/kg for the higher dose

The 3 keto carbofuran level showed an increasing trend reaching the highest (0 129 mg/kg) on the 3rd day when applied at the lower dose and on the 7th day (0 318 mg/kg)when applied at the higher dose By the 28th day the presence of 3 keto carbofuran was not detectable in the leaf samples for both the doses tried

Regarding the level of total carbofuran the highest concentration was detected on the 3rd day after treatment for both the doses and the values were 0 494 and 0 934 mg/kg for the lower and higher dose respectively A declining trend was noticed after the third day for both the doses By the 28th day the contents decreased to very low values of 0 027 and 0 067 mg/kg when applied at 0 5 and 1 5 kg ai/ ha respectively

Table 4 **Residues of carbofuran and its metabolites in the vines of cucumber plants treated in the field at the vining stage of the crop**

Days after treatment	mean level of residues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg ai / ha		
1	0 203 (+0 015)	0 309 (+0 016)	0 249 (+0 025)	0 761 (±0 026)
3	0 175 (±0 019)	0 288 (±0 013)	0 213 (+0 021)	0 676 (±0 02)
7	0 105 (+0 014)	0 171 (+0 017)	0 124 (+0 013)	0 400 (±0 009)
14	0 063 (+0 012)	0 141 (+0 027)	0 096 (+0 015)	0 300 (+0 020)
21	0 033 (+0 010)	0 065 (+0 017)	0 043 (+0 014)	0 041 (±0 020)
28	ND	0 035 (+0 022)	ND	0 035 (+0 022)
		1 5 kg ai / ha		
1	0 472 (+0 046)	0 763 (+0 031)	0 601 (+0 017)	1 837 (+0 032)
3	0 305 (+0 018)	0 591 (+0 012)	0 454 (+0 016)	1 345 (+0 01)
7	0 149 (+0 01)	0 470 (+0 021)	0 378 (+0 020)	0 997 (+0 037)
14	0 116 (+0 010)	0 266 (+0 022)	0 183 (+0 016)	0 565 (+0 017)
21	0 052 (+0 019)	0 09 (+0 01)	0 069 (±0 016)	0 211 (±0 01)
28	ND	0 062 (+0 02)	ND	0 062 (+0 029)

ND Non Detectable

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As in the case of the parent compound the level of 3 OH carbofuran was also found to be maximum in the vines on the first day after treatment for both the doses the levels being 0 309 and 0 763 mg/kg respectively These values decreased considerably to 0 035 and 0 062 mg/kg by the 28th day for the lower and higher dose respectively

A similar declining trend was noticed in the case of 3 keto carbofuran also with the highest level observed on the first day after treatment for both the doses The values were 0 249 and 0 601 mg/kg for the lower and higher dose respectively A gradually declining trend was followed thereafter upto the 21st day for both the doses The residue levels on the 3rd 7th 14th and 21st day were 0 213 0 124 0 096 and 0 043 mg/kg for the lower dose and for the higher dose the corresponding values were 0 454 0 378 0 183 and 0 069 mg/kg The metabolite 3 keto carbofuran was detected in the vine samples only up to the 21st day after treatment for both the doses

The maximum concentration of total carbofuran residues was detected in the vines on the first day after treatment for both the doses the initial levels being 0 761 and 1 837 mg/kg when applied at 0 5 and 1 5 kg ai/ha respectively The total

carbofuran in the vines was accounted by 3 OH fraction alone on the 28th day for both the doses tried The relative values were 0 035 and 0 062 mg/kg for the lower and higher dose respectively The values on 3rd 7th 14th and 21st day after treatment were 0 676 0 400 0 300 and 0 041 mg/kg respectively for the lower dose and for the higher dose the corresponding figures were 1 345 0 997 0 565 and 0 211 mg/kg respectively

3 5 Metabolism of carbofuran in the vines of cucumber Plants when applied at the flowering stage of the crop

The data presented in Table 5 indicate the presence of metabolites namely 3 OH carbofuran 3 keto carbofuran along with pure carbofuran in the vine samples on the first day after treatment onwards when treated at the flowering stage of the crop at two doses The metabolites were present in varying proportions in the vine samples at different intervals

As in the case of the sowing and vining stages the maximum extent of pure carbofuran was detected in the vines on the first day after treatment for both the doses The residues observed at 0 5 and 1 5 kg ai/ha were 0 227 and 0 365 mg/kg respectively which got reduced to 0 041 and 0 039 mg/kg by the 21st day after

Table 5 Residues of carborfuran and its metabolites in the vines of cucumber plants treated in the field at the flowering stage of the crop

Days after treatment	mean level of residues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg ai / ha		
1	0 227 (+0 042)	0 398 (+0 137)	0 369 (+0 074)	0 995 (±0 252)
3	0 177 (+0 013)	0 243 (+0 040)	0 237 (+0 061)	0 657 (±0 025)
7	0 151 (+0 012)	0 176 (+0 014)	0 216 (+0 012)	0 542 (+0 010)
14	0 047 (±0 019)	0 183 (+0 028)	0 048 (±0 011)	0 279 (±0 039)
21	0 041 (±0 013)	0 104 (+0 018)	0 027 (+0 010)	0 172 (+0 037)
28	ND	0 040 (+) 010)	ND	0 040 (±0 010)
		1 5 kg ai / ha		
1	0 365 (+0 037)	0 705 (+0 025)	0 303 (±0 017)	1 373 (+0 01)
3	0 175 (±0 028)	0 338 (+0 064)	0 268 (+0 034)	0 781 (+0 038)
7	0 163 (+0 007)	0 268 (+0 020)	0 183 (±0 015)	0 614 (+0 020)
14	0 041 (+0 017)	0 266 (+) 014)	0 165 (+0 011)	0 472 (+0 00J)
21	0 039 (+0 020)	0 077 (+0 007)	0 056 (+0 015)	0 172 (±0 014)
28	0 025 (+0 017)	0 035 (+0 014)	ND	0 060 (+0 030)

ND Non Detectable

treatment On the 28th day after treatment pure carbofuran was not detectable in the vine samples when applied at 0 5 kg ai/ha whereas a level of 0 025 mg/kg could be detected in the plants treated with 1 5 kg ai/ha

In the vine samples conversion of carbofuran to 3 OH carbofuran was initiated on the first day after treatment itself The highest level of 3 OH carbofuran in the vines on the first day after treatment indicated that active conversion took place on the first day itself The corresponding levels for 0 5 and 1 5 kg ai/ha were 0 398 and 0 705 mg/kg respectively A gradual decrease was noticed thereafter and by the 28th day the level reached to 0 040 and 0 035 mg/kg for the lower and higher dose respectively

As in the case of pure and 3 OH forms the 3 keto form also followed the same pattern the highest levels (0 369 mg/kg for lower and 0 303 mg/kg for higher dose) being recorded on the first day after treatment The residues reached non detectable level by the 28th day for both the lower and higher dose

The total carbofuran content of the vines was maximum on the first day after treatment for both the doses The corresponding values at 0 5 and 1 5 kg ai/ha were 0 995 and 1 373 mg/kg

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respectively The levels reached to 0 040 and 0 060 mg/kg by the 28th day for the lower and higher dose respectively On the 28th day after treatment the total residue in the vines was accounted by the 3 OH fraction alone when applied at 0 5 kg ai/ha Whereas parent compound as well as 3 OH carbofuran were noted in the case of treatment at 1 5 kg ai/ha

3 6Metabolism of carbofuran in cucumber fruits when applied at the vining stage of the crop.

The metabolism and level of residues of carbofuran in cucumber fruits when applied at the vining stage of the crop at doses of 0 5 and 1 5 kg ai/ha are presented in Table 6 The metabolites namely 3 OH carbofuran 3 keto carbofuran along with the parent compound were detected in the fruit samples collected from 14 DAT onwards (Fruits were available for analysis only from 14th day onwards)

The level of pure carbofuran in the fruits at 14th and 21st days after treatment were 0 151 and 0 111 mg/kg for the lower dose and the corresponding values were 0 204 and 0 125 mg/kg for the higher dose respectively The presence of the pure form of carbofuran could not be detected in fruit samples collected at

Table 6 Residues of carbofuran and its metabolites in the cucumber fruits when treated at the vining stage of the crop

Days after treatment	Mean level of res dues (mg/kg)			
	Pure carbofuran	3 0H carbofurn	3 keto carbofuran	Total carbofuran
		0 5 kg ai/ha		
14	0 151 (+0 018)	0 065 (+0 01)	0 02 (+0 008)	0 237 (+0 007)
21	0 111 (+0 017)	0 025 (+0 009)	0 032 (±0 011)	0 169 (±0 009)
28	ND	ND	0 034 (+0 017)	0 034 (+0 017)
		1 5 kg a /ha		
14	0 204 (+0 02)	0 076 (±0 01)	0 136 (±0 017)	0 417 (+0 417)
21	0 125 (+0 01C)	0 025 (+0 011)	0 045 (±0 018)	0 196 (+0 018)
28	ND	0 021 (± 0 013)	ND	0 021 (+0 013)

ND Non Detectable

43

28 DAT for both the doses

As in the case of pure carbofuran the 3-OH carbofuran also showed a decreasing trend reaching non detectable level by the 28th day for the lower dose whereas a residue level of 0 021 mg/kg could be detected in the fruits when the crop was treated with the higher dose

The level of 3-keto carbofuran in the fruits showed an increasing trend from 14th to 28th day after harvest for the lower dose But in the higher dose a decreasing trend was observed reaching to the non detectable level by the 28th day after treatment

Regarding total carbofuran residues in the fruit samples a decreasing trend was noticed, from the 14th to 28th day after application for both the doses The levels on 14 21 and 28 days were in the order of 0 237 0 169 and 0 034 mg/kg in the case of lower dose whereas the degradation was in the order of 0 417, 0 196 and 0 021 mg/kg in the case of higher dose of carbofuran On the 28th day when applied at 0 5 kg ai/ha the total carbofuran was accounted by 3-keto carbofuran fraction alone whereas for the higher dose it was accounted by 3-OH carbofuran alone

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3 7 Metabolism of carbofuran in the whole fruit samples when applied at the flowering stage of the crop

The data presented in Table 7 indicate the presence of metabolites namely 3 oH carbofuran 3 keto carbofuran along with the parent compound pure carbofuran in whole fruit samples on the first day after treatment onwards when treated at the flowering stage of the crop at two doses

The initial level of pure carbofuran in the fruit samples when applied at 0 5 and 1 5 kg ai/ha were 0 065 and 0 189 mg/kg which got increased to 0 107 and 0 212 mg/kg by the seventh day for the lower and higher doses respectively By the 28 day after treatment (DAT) these levels got reduced to 0 037 and 0 067 mg/kg for the doses 0 5 and 1 5 kg ai/ha respectively

As in the case of pure carbofuran the 3 OH carbofuran also showed an increasing trend from the first day to the 7th day after treatment for both the doses tried The residue level in fruits harvested on 7th day after treatment for the lower and higher doses were 0 527 and 0 715 mg/kg respectively The residues detected on 14 21 and 28 DAT were 0 227 0 098 and 0 066 mg/kg respectively for the lower dose and the corresponding

Table 7 Residues carbofuran and its metabolites in the whole fruits when treated at the flowering stage of the crop

Days after treatment	mean level of res dues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg al / ha		
1	0 065 (+0 018)	0 159 (+0 013)	0 127 (±0 022)	0 352 (±0 035)
3	0 057 (+0 011)	0 192 (+0 021)	0 149 (±0 015)	0 398 (+0 021)
7	0 107 (+0 011)	0 527 (+0 089)	0 287 (±0 028)	0 921 (+0 107)
14	0 101 (+0 018)	0 227 (+0 045)	0 130 (+0 026)	0 457 (±0 062)
21	0 054 (+0 012)	0 098 (±0 019)	0 071 (±0 016)	0 223 (+0 031)
28	0 037 (+0 009)	0 066 (+ 018)	ND	0 103 (+0 030)
		1 5 kg al / ha		
1	0 189 (+0 015)	0 189 (±0 02)	0 083 (+0 014)	0 461 (±0 051)
3	0 138 (+0 038)	0 192 (±0 018)	0 099 (±0 021)	0 429 (+0 045)
7	0 212 (+0 053)	0 715 (+0 181)	0 311 (+0 092)	1 238 (±0 180)
14	0 138 (+0 040)	0 243 (±0 060)	0 188 (+0 034)	0 569 (±0 051)
21	0 100 (+0 019)	0 142 (±0)	0 152 (±0 011)	0 394 (± 0031)
28	0 067 (+0 016)	0 081 (+ 020)	ND	0 147 (+0 020)

ND Non Detectable

levels for the higher dose were 0 243, 0 142 and 0 081 mg/kg respectively

A similar trend was seen in the case of 3 keto carbofuran also reaching the highest value on the 7th day after treatment for both the doses which got reduced to levels below detectable limit by the 28th day after treatment for both the doses

Regarding total carbofuran residues in the fruit samples the initial levels were 0 352 and 0 461 mg/kg which got increased to 0 962 and 1,238 mg/kg when applied at 0 5 and 1.5 kg ai/ha on the third day

Total carbofuran residues observed on 14 and 21st days after treatment were 0 457,0 223 for the lower dose and for the higher dose the corresponding values were 0 569 and 0 394 mg/kg respectively On the 28th day after treatment the residues were 0 07 and 0 108 mg/kg for the doses of 0 5 and 1 5 kg ai/ha respectively.

3 8 Metabolism of carbofuran in the peeled fruit samples when applied at the flowering stage of the crop

The active metabolism and degradation of carbofuran in peeled

Table 8 Residues carbofuran and metabolites in the peeled cucumber fruits when treated at the flowering stage of the crop

Days after treatment	mean level of residues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
		0 5 kg al / ha		
1	0 075 (+0 018)	0 290 (+0 08)	0 170 (+0 039)	0 536 (±0 021)
3	0 120 (+0 030)	0 139 (+ 43)	0 057 (±0 025)	0 318 (±0 021)
7	0 127 (+0 05?)	0 324 (+0 038)	0 233 (+0 108)	0 678 (±0 012)
14	0 088 (+0 036)	0 090 (+ 0041)	0 179 (±0 042)	0 358 (±0 044)
21	0 060 (+0 050)	0 0178 (+0 010)	0 048 (+0 017)	0 193 (+0 042)
28	ND	0 070 (+ 0 0)	ND	0 07 (+0 015)
		1 5 kg al / ha		
1	0 161 (+0 08?)	0 270 (+ 43)	0 107 (+0 038)	0 536 (+0 047)
3	0 119 (+0 02)	0 252 (±0 175)	0 305 (+0 141)	0 676 (+0 01?)
7	0 133 (+0 022)	0 400 (+ 098)	0 370 (±0 095)	0 903 (+0 010)
14	0 067 (+0 027)	0 278 (+0 174)	0 214 (+0 062)	0 560 (±0 035)
21	0 054 (+0 028)	0 070 (+0)	0 079 (+0 054)	0 303 (±0 13?)
28	0 043 (+0 021)	0 065 (±0 0?)	ND	0 108 (+0 0 34)

ND Non Detectable

fruit samples when applied at 0 5 and 1 5 kg ai/ha at the flowering stage of the crop is presented in Table 8 The results indicated that active metabolism of the compound started on the first day after treatment onwards for both the doses The metabolites namely 3 OH carbofuran 3 keto carbofuran and pure carbofuran were present in the fruit samples on the first day itself at varying proportions

The initial levels of pure carbofuran for the lower and higher doses were 0 075 and 0 161 mg/kg respectively As in the case of whole fruit samples maximum content of pure carbofuran was noticed in fruits collected at the 7th day itself even after peeling But when applied at 1 5 kg ai/ha the peak level was observed on the first day after treatment which got reduced to 0 054 mg/kg by the 21st day The level on the 28th DAT for the higher dose was 0 043 mg/kg but for the lower dose the residue was not detectable

The level of 3 OH carbofuran showed a decreasing trend from the first day to the third day reaching the maximum on the seventh day for both the doses A decreasing trend was noticed thereafter By the 28th day the levels reached 0 07 and 0 065 mg/kg for the lower and higher dose respectively The level of

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3 keto carbofuran showed a decreasing trend from the first day to the third day and increased thereafter reaching the maximum on the seventh day after treatment for the lower dose But in the case of higher dose a steadly increasing trend was observed from the first day onwards reaching the maximum on the seventh day On the 28th day after treatment the levels were not detectable for both the doses

Regarding the total residues the highest value was obtained on the 7th days after treatment for both the doses The residue levels were 0 678 and 0 903 for the lower and higher dose respectively

The residue levels in peeled fruits were above the MRL upto the 14th day after treatment when the crop was treated with the lower dose but in the case of higher dose upto the 21st day the residues were above the MRL

3 9 Metabolism of carbofuran in the various portions of cucumber fruits when treated at the flowering stage of the crop

The metabolism and level of residues in various fruit portions viz top middle and basal when treated at the flowering stage of the crop is presented in Table 9 The different portions were analysed seperately at various intervals The

Table 9 Residues of carbofuran and its metabolites in the various portions of cucumber fruits when treated at the flowering stage of the crop

Days after treatment	Portion of the fru t	mean level of res dues (mg/kg) Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
7	Top	0 202 (+0 050)	0 782 (+0 003)	0 384 (±0 006)	1 368 (+0 181)
14		0 208 (+0 002)	0 133 (±0 072)	0 197 (±0 026)	0 538 (+0 100)
21		0 147 (+0 040)	0 08 (+0 060)	0 084 (±0 032)	0 311 (+0 083)
7	Middle	0 212 (+0 053)	0 715 (+0 047)	0 311 (+0 005)	1 198 (+0 010)
14		0 0246 (+0 100)	0 058 (+0 006)	0 208 (±0 050)	0 513 (+0 135)
21		0 084 (+0 013)	0 042 (+0 022)	0 072 (+0 021)	0 198 (+0 009)
7	Basal	0 133 (+0 022)	0 400 (+0 008)	0 401 (+0 030)	0 934 (+0 003)
14		0 137 (+0 083)	0 131 (+0 076)	0 216 (+0 081)	0 484 (+0 054)
21		0 133 (±0 030)	0 018 (+0 002)	0 034 (±0 009)	0 185 (+0 028)

ND Non Detectable

results showed that the highest level of total carbofuran was detected in the top portion of the fruit The levels on the seventh fourteenth and twenty first days after treatment where 1 368 0 538 and 0 311 mg/kg respectively This was followed by the middle and basal portions The corresponding levels in the middle portion where 1 198 0 513 and 0 198 mg/kg respectively While in the basal portion the levels were 0 934 0 484 and 0 185 mg/kg respectively The metabolites namely 3-OH carbofuran 3 keto carbofuran and the parent compound were present in varying proportions in the different portions tested

4 1 Metabolism of carbofuran in the flesh and placenta of cucumber fruits when treated at the flowering stage of the crop at 1.5 kg ai/ha

The metabolism and extent of residues in the flesh and placenta of cucumber fruits when applied at the flowering stage of the crop at 1 5 kg ai/ha is presented in Table 10 Samples of flesh and placenta (inner core + Seeds) were subjected to chemical analysis separately at different intervals of 7 14 and 21 days after application of the insecticide The metabolites namely 3 OH carbofuran 3 keto carbofuran and the parent compound pure carbofuran were present in the flesh and placenta

Table 10 Residues of carbofuran and its metabolites in the flesh and placenta of cucumber fruits when treated at the flowering stage of the crop @1 5 kg al/ha

Portion of the fru t	days after treatment	mean level of residues (mg/kg) pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total carbofuran
flesh	7	0 212 (+0 053)	0 715 (+0 181)	0 311 (+0 099)	1 238 (±0 186)
	14	0 138 (+0 01J)	0 243 (+0 012)	0 188 (±0 011)	1 394 (+0 031)
	21	0 100 (+0 019)	0 142 (+0 012)	0 152 (±0 011)	0 394 (±0 031)
Placenta	7	0 157 (±0 030)	0 366 (±0 0J)	0 248 (+0 050)	0 771 (+0 136)
	14	0 130 (+0 0400	0 106 (+0 020)	0 136 (±0 023)	0 373 (+0 015)
	21	0 084 (+0 060)	0 072 (+0 030)	0 189 (+0 032)	0 345 (±0 030)

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in all these intervals tested The results indicated that the residues of total carbofuran and the metabolites were invariably high in the flesh rather than in the placenta in all the intervals tested Thus the total carbofuran residues in the flesh at intervals of 7 14 and 21 DAT were 1 238 0 569 and 0 394 mg/kg respectively where as on the placenta the corresponding levels were 0 771 0 373 and 0 345 mg/kg respectively

4 2 Metabolism of carbofuran in cucumber fruits when stored unde refrigeration

The metabolism and level of residues in cucumber fruits when stored under refrigeration for different periods are presented in Table 11 The fruit samples collected from crop treated at the higher dose alone were subjected to refrigeration and samples were drawn at 0 1 4 5 7 and 10 day interval and the degradation was studied The results indicated that the metabolites namely 3 OH carbofuran 3 keto carbofuran and pure carbofuran were present in all the intervals

The initial concentration of pure carbofuran was 0 068 mg/kg A gradual reduction in residues was noticed in all the intervals reaching 0 025 mg/kg by the 10th day interval The levels on the 1st 4th 5th and 7th days were 0 059 0 045 0 035 and 0 028 mg/kg respectively

Table 11 Residues carbofuran and its metabolites in cucumber fruits stored under refrigeration at different intervals

Period under refr geration (Days)	mean level of residues (mg/kg)			
	Pure carbofuran	3 OH carbofuran	3 keto carbofuran	Total Carbofuran
0	0 068 (+0 025)	0 061 (+0 022)	0 172 (+0 037)	0 301 (+0 084)
1	0 059 (+0 025)	0 038 (+0 017)	0 150 (+0 05)	0 247 (±0 084)
4	0 045 (+0 020)	0 044 (+0 014)	0 130 (+0 024)	0 218 (±0 037)
5	0 035 (+0 010)	0 037 (+0 021)	0 075 (+0 009)	0 147 (±0 005)
7	0 028 (+0 013)	0 034 (+0 013)	0 070 (±0 010)	0 133 (±0 007)
10	0 025 (+0 011)	0 021 (+0 013)	0 047 (±0 010)	0 094 (+0 012)

Table 12 Waiting period of carbofuran in cucumber fruits when applied at the flowering stage of the crop

Kind of fruit	Dose (kg ai/ha)	Waiting period T(tol) days	R^2	Regression equation
Whole fruit	0 5	24 5	0 5	$Y = 0\ 4074 + 0\ 0356x_1\ 0\ 0018x_2$
	1 5	26 1	0 5	$Y = 0\ 4831 + 0\ 0544x_1\ 0\ 0025x_2$
Peeled fruit	0 5	23 2	0 7	$Y = 0\ 48774 + 0\ 0038x\ -0\ 007x_2$
	1 5	26 2	0 8	$Y = 0\ 6219 + 0\ 0210x_1 - 0\ 0015x_2$

In the case of 3-OH carbofuran the highest level (0 061 mg/kg) was observed on the first day followed by a reduction to 0 044 mg/kg on the fourth day reaching 0 021 mg/kg on the 10th day of storage

As in the case of pure carbofuran a similar trend was observed in the case of 3-keto form also From the initial concentration of 0 172 mg/kg the level got reduced to 0 047 mg/kg by the 10th day

The initial concentration of total carbofuran was 0 301 mg/kg which got reduced to 0 247 mg/kg on the first day and 0 218 mg/kg day on the 4th day of storage under refrigeration From the fifth day of storage onwards, the total residues of carbofuran observed in fruits were below the MRL of 0 2 ppm the values being 0 147, 0 133 and 0 094 mg/kg on 5,7 and 10 days of storage

Waiting period of carbofuran in cucumber fruits when applied at the flowering stage of the crop

Carbofuran was applied at doses 0 5 and 1 5 kg ai/ha at the flowering stage of the crop and the waiting periods were worked out by means of regression equations (Table 12) Since the MRL has not been fixed for carbofuran in vegetables in the present study the waiting period was fixed taking in to consideration the MRL of 0 2 ppm fixed for the grain crops Thus in the present study the results indicated that a waiting period of 25 and 26 days should be

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recommended for the lower and higher dose respectively. Since cucumber fruits are harvested at 20-30 days after flowering of the crop, the use of carbofuran granules at the flowering stage of the plant should be avoided to prevent the residue hazard

DISCUSSION

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DISCUSSION

5 1 Carbofouran is a broad spectrum insecticide widely used for the control of a variety of pests affecting the crop plants (Mathur et al 1974) In cucurbitaceous vegetables it is highly effective for the control of fruits flies and other sucking pests But the application of the chemicals is recommended only at the time of sowing in vegetables (KAU 1989) The farmers are extensively using the chemical even at the fruit setting period due to its effectiveness in controlling various pests A recent survey conducted to assess the content of carbofuran in market samples of vegetables showed definite evidence of application of carbofuran at rates higher than the recommended rate close to the fruiting stage (Rajendran et al 1991) Information on the chemodynamics of carbofuran in vegetables and the influence of the growth stage of the crop on the uptake and metabolism of the chemical is scanty and meagre. The uptake, translocation and metabolism of the compound when applied to cucumber plants at different growth stages especially at the flowering stage of the crop are discussed hereunder

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Uptake, metabolism and persistence of carbofuran in cucumber plants treated at three different growth stages viz sowing, vining and flowering

Several studies have shown that the principal metabolic pathways of carbofuran include hydrolysis oxidation and conjugation (Dorough 1968 Metcalf 1968 Kuhr 1970 Ashworth 1972 Mohammed Ali 1978 and Singh & Kalra 1992) The major metabolites detected in different crop plants were 3 OH carbofuran 3 keto carbofuran and their corresponding phenols (Dorough 1968 Metcalf et al 1968 Pree et al 1974 Huynh & Morallo 1975 and Singh & Kalra 1992) However the extent of metabolism of carbofuran in cucurbitaceous vegetables are not well determined

Previous workers have demonstrated that carbofuran persisted for a period of 45 days in cow pea pods (Nanda Kumar 1981) more than 75 days in brinjal (Mithyantha et al 1978) 60 80 days in sorghum (Srivastava 1976) & 118 days in potato (Misra & Dikshit 1991) However studies conducted under the All India Co ordinated Project on Pesticide Residues at Vellayani centre revealed that carbofuran residues reached below the maximum residue limit of 0 2 ppm within 23 days in cucumber fruits (Beevi et al 1991a) and

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within 22 days in bittergourd fruits (Beevi et al 1991b)
Hence in the present investigation the sampling and analysis of carbofuran residues were made for a maximum period of 28 days after application

5 2 Metabolism and persistence of carbofuran in cucumber leaves when treated at three different growth stages

The data presented in Table 1 indicated that the highest level of the parent compound pure carbofuran was observed on the first day after treatment in the leaf samples for both the doses when applied at sowing But the metabolites namely 3 OH carbofuran and 3 keto carbofuran were found at the maximum concentration on the third day after treatment for both the doses tested The concentration of pure 3 OH and 3 keto carbofuran constituted 14 47 43 0 and 42 5 percentage of the total residues on the third day for the lower dose and the corresponding percentages for the higher dose were 9 3 55 6 and 35 09 respectively

The initial level of total carbofuran in the leaves at sowing was 0 611 mg/kg for the lower dose From the initial level an increase of 1 63 times was observed on the 3rd day for the lower dose and the corresponding increase for the higher dose was 1 98 times The percentage reduction on the 28th day from the peak

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level was 94 and 90% for the lower and higher doses respectively On the 28th day total carbofuran was accounted by 3 OH carbofuran alone for the lower dose while for the higher dose the presence of pure and 3 OH carbofuran were detected

When carbofuran was applied at the vining stage of the crop (Table 2) the maximum level of pure carbofuran was seen in the leaves on the first day as in the case of the treatment done at the sowing stage As against pure carbofuran the peak level of metabolites was detected on the third day after treatment for both the doses Pure 3 OH and 3 keto carbofuran constituted 16 29 53 48 and 30 22 per cent of the total on the third day for the lower dose whereas when applied at 1 5 kg ai/ha the corresponding percentages were 11 35 61 5 and 27 1 respectively Regarding total carbofuran residues the highest level was observed on the third day for both the lower and higher dose The residue level on the third day for the higher dose was about three times more than the level on the same day for the lower dose On 28 DAT percentage reduction of 96 74 and 95 11 over the third day was observed for the lower and higher dose respectively The total carbofuran on the 28 DAT was accounted by 3 OH fraction alone for the lower dose whereas for the higher dose the presence of both 3 OH and 3 keto carbofuran were

detected in the leaf samples The parent compound became almost completely dissipated before 28 DAT for both the doses tested

The results in Table 3 clearly showed that the degradation pattern of pure carbofuran in the leaves when applied at the flowering stage of the crop was exactly similar to that of the sowing stage with the presence of detectable residues for the higher dose on the 28 DAT

As against the sowing and vining stages the maximum level of 3 keto carbofuran was detected on the 7th DAT for the higher dose of 1 5 kg ai/ha The results also showed that when carbofuran was applied at flowering the active conversion to 3 OH carbofuran was lesser for the higher dose when compared with the lower dose

Regarding the total residues similar pattern was followed as in the case of the earlier stages with the peak level reaching on 3 DAT Upto 94 5 percent degradation was seen on 28th DAT from the highest level for the lower dose and the corresponding percentage for the higher dose was 92 8% The total carbofuran on the 28 DAT was accounted by 3 OH carbofuran alone for the lower dose while for the higher dose both pure and 3 OH carbofuran were together responsible The percentage degradation was found highest in the

intervals starting from the 21st DAT when compared with other intervals taken for both the doses The corresponding values were 81 7 and 70 9 per cent for the lower and higher dose respectively

Translocation and degradation of carbofuran in the leaves of cucumber plants as influenced by the different growth stages of the crop is illustrated in the fig The plants treated at the vining and sowing stages translocated maximum amount of carbofuran within 3 days after application while the plants treated at the flowering stage translocated considerably lesser amount of carbofuran

5 3 Metabolism and persistence of carbofuran in cucumber vines when treated at vining and flowering stages of the crop.

Metabolism of carbofuran in cucumber vines when applied at the vining stage of the crop (Table 4) revealed that maximum level of residues was present in the first day after application as evidenced by the peak level of metabolites and parent compound followed by a gradual decline upto 28th DAT for both the doses

This indicated that maximum metabolism and highest level of absorption took place in the vines on the first day itself Pure

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3 OH and 3 keto carbofuran constituted 26 6 40 6 and 32 7 percent of the total residues on the first day for the lower dose whereas the corresponding percentages for the higher dose were 25 69 41 53 and 32 7 respectively Among the metabolites tested 3 OH carbofuran was found to be the one metabolite observed with maximum concentration for both the doses This indicates that active conversion to 3 OH carbofuran occurs immediately after absorption by the plant

The highest level of total carbofuran was observed in the vines on the first day after treatment for both the doses tested The percentage degradation on the 28th day over the peak level was 95 4 and 96 6 when treated at 0 5 and 1 5 kg ai/ha respectively On the 28th DAT the total carbofuran was accounted by 3 OH fraction alone for the two doses tested

The pattern of metabolism and dissipation of carbofuran in the vines when applied at the flowering stage is similar to that of the vining stage (Table 5) The peak level of metabolites along with the parent compound was detected on the first day after treatment for both the doses

The contribution of pure 3 OH and 3 keto carbofuran towards total residue was 22 8 40 0 and 37 0 percent on the first DAT

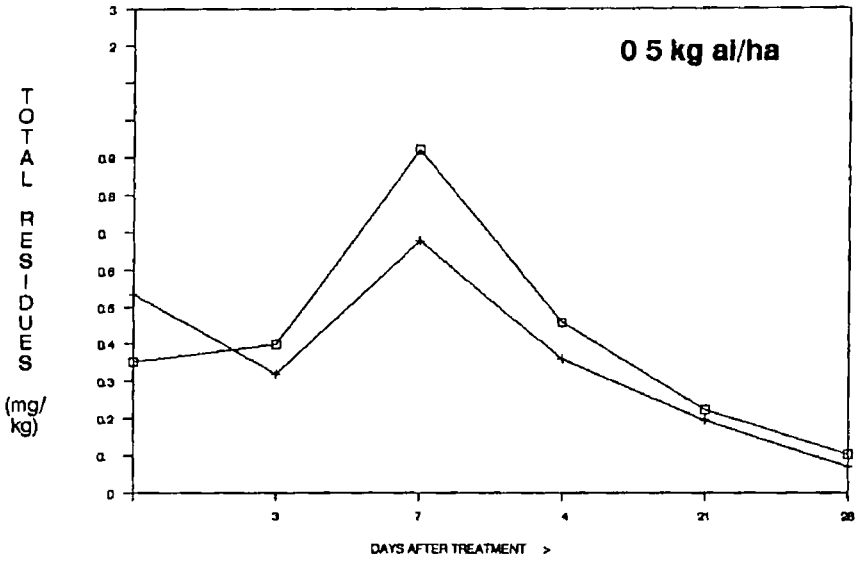
for the lower dose where as the corresponding percentages being 26 5 51 3 and 22 0 respectively for the higher dose

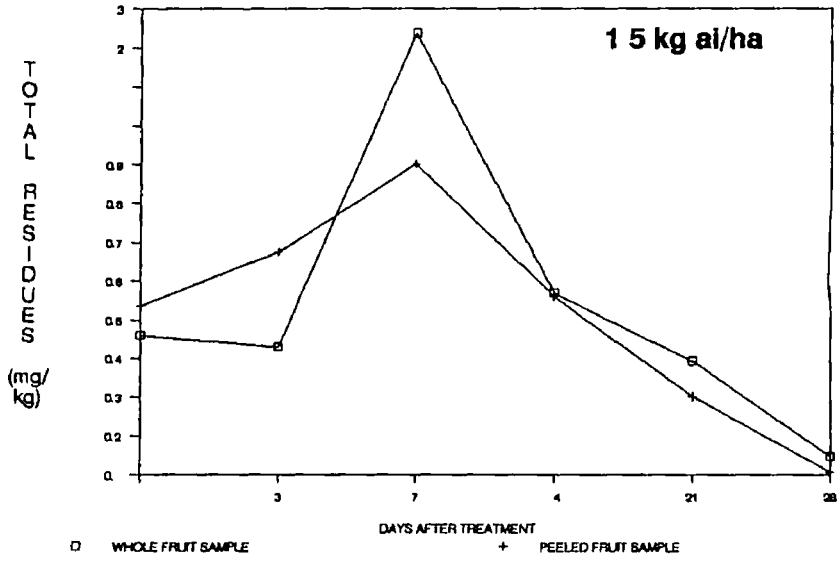
On the 28th day the total carbofuran was accounted by 3 OH carbofuran alone for the lower dose as in the case of vining stage whereas the presence of pure and 3 OH carbofuran was detected in the vine samples tested for the higher dose

5 4 Effect of peeling on the degradation of residues of carbofuran in cucumber fruits when applied at the flowering stage.

The data presented in Table 7 and 8 and fig 1 show the effect of peeling on the removal of carbofuran residues The highest level of total residues was obtained on 7 DAT in case of both the whole fruit samples and peeled ones when applied at 0 5 and 1 5 kg ai/ha In both the cases the metabolism was initiated on the first day itself as in the case of leaf and vine samples which was evidenced by the presence of metabolites along with the parent compound The presence of peak level of total carbofuran on the 7th day indicated that active metabolism took place in the fruits in a later stage than vines and leaves where the maximum level was detected on the 1st and 3rd day after

Fig 1 EFFECT OF PEELING ON THE REDUCTION OF TOTAL CARBOFURAN RESIDUES



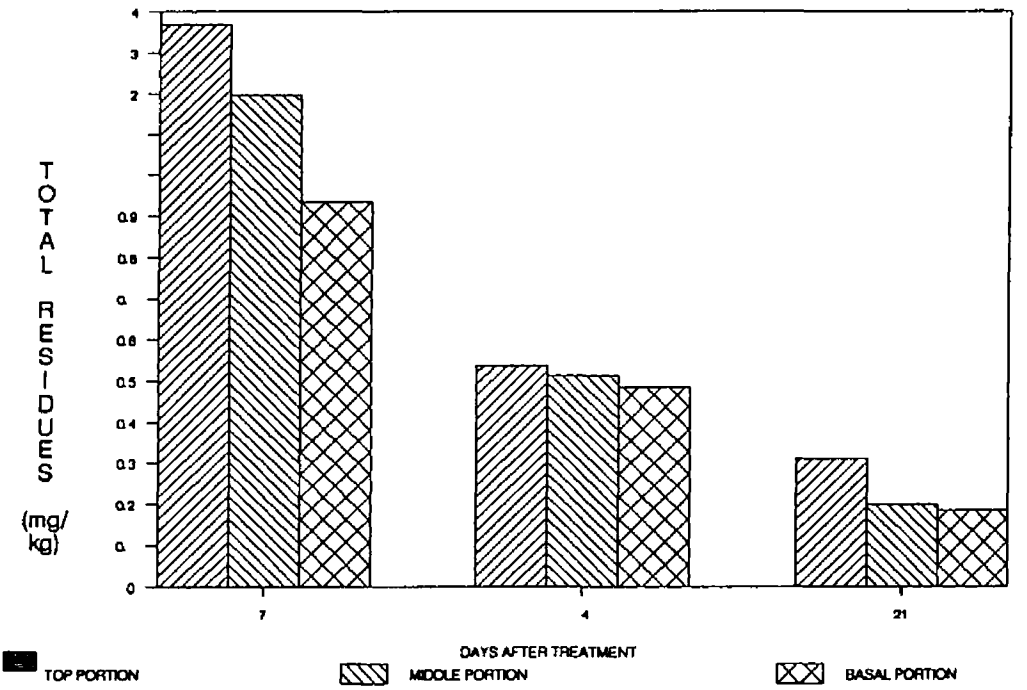


□ WHOLE FRUIT SAMPLE + PEELED FRUIT SAMPLE

application respectively The total residue levels were 4 6 and 3 4 times above the MRL of 0 2 PPM on 7 DAT for whole fruit and peeled samples respectively for the lower dose When applied at 1 5 kg ai/ha the levels were 6 2 and 4 5 times above the MRL on the same day The percentage degradation on the 28 DAT over the peak level did not show much variation in the whole and peeled samples for both the doses tested

On the 28th day after treatment total carbofuran was accounted by pure and 3 OH carbofuran for both the doses for whole fruit samples But in the case of peeled fruits only 3 OH carbofuran was present on 28 DAT for the lower dose whereas both pure and 3 OH carbofuran could be detected when applied at 1 5 kg ai/ha The results (Fig 1) substanciate the findings of Awasthi and Mishra (1978) who reported that washing and peeling considerably reduced the carbofuran residues in potato tubers Studies by Finalyson et al (1976) also showed that greater quantities of residues were accumulated in the peel portion than in the pulp portion of carrot tubers

Fig 2 RESIDUES OF TOTAL CARBOFURAN IN THE TOP MIDDLE AND BASAL PORTION OF CUCUMBER FRUITS WHEN TREATED AT THE FLOWERING STAGE OF THE CROP



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5 5 The distribution of carbofuran residues in different portions of cucumber fruits (top, middle and basal) when treated at the flowering stage of the crop.

The results presented in Table 9 indicate the distribution pattern of carbofuran residues in different portions of the fruit The metabolites 3 OH carbofuran and 3 keto carbofuran along with the parent compound were present in all the three portions of the fruit tested On the 7th and 14th DAT the highest concentration of total residues (1 368 and 0 538 mg/kg respectively) was seen on the top portion of the fruit followed by middle and basal portions On the 21st day also the same trend was noticed (Fig 2)

This confirms the fact that accumulation of residues was more in the top portion of the fruit than the rest of the portions This was in conformity with the findings of Finalyson et al (1976) who reported that the accumulation of residues was more in the top portion of carrot tubers than in the lower portion

5 6 Comparison of carbofuran residues in the flesh and placenta of the fruits when applied at the flowering stage of the crop.

The level of residues of carbofuran in the flesh and placenta of the cucumber fruits when treated at the flowering stage of the

Fig 3 RESIDUES OF TOTAL CARBOFURAN IN THE FLESH AND PLACENTA OF CUCUMBER FRUITS WHEN TREATED AT THE FLOWERING STAGE OF THE CROP

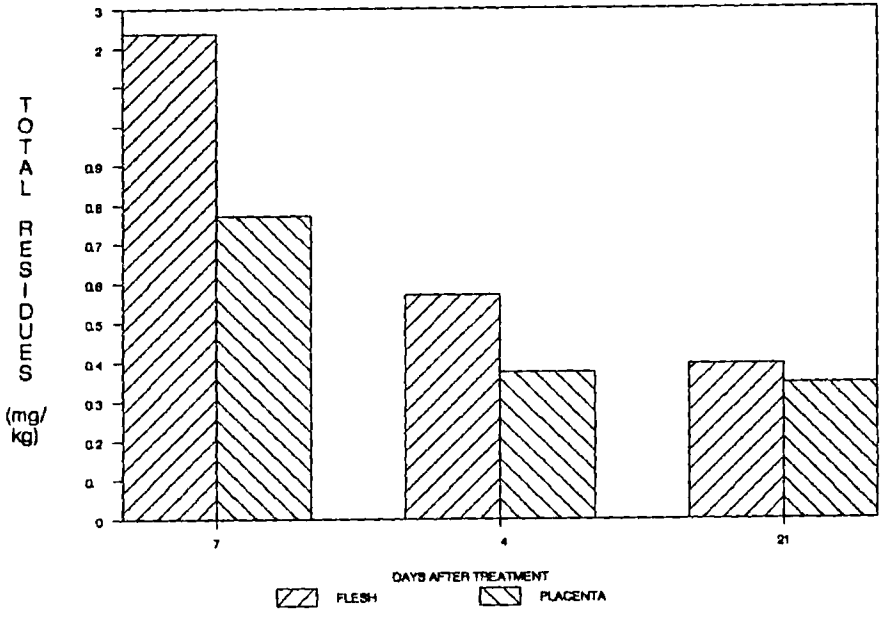
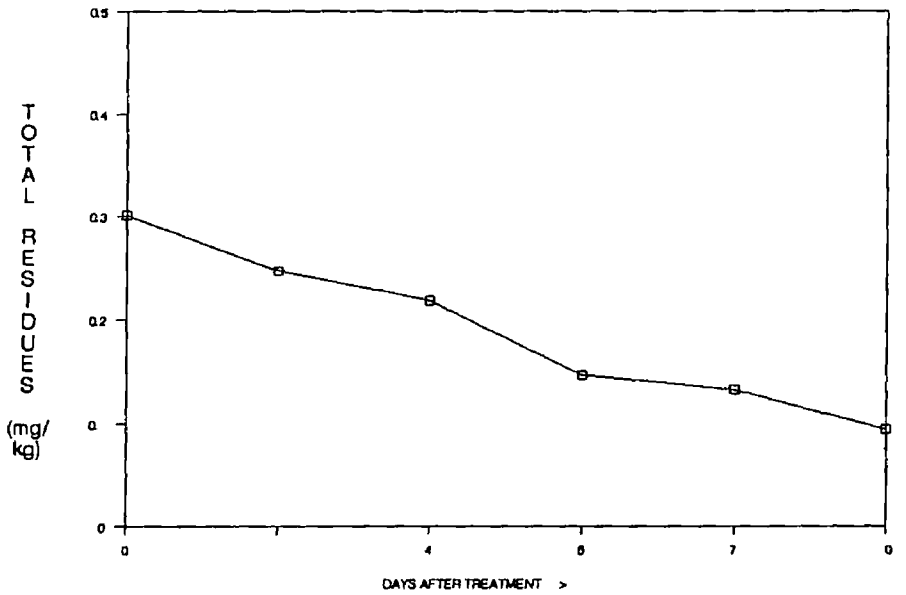


Fig 4 EFFECT OF STORAGE UNDER REFRIGERATION ON THE DEGRADATION OF TOTAL CARBOFURAN RESIDUES IN CUCUMBER FRUITS



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crop is presented in table 10 Fig 3 shows that maximum concentration of total carbofuran was detected in the flesh rather than in the placenta and seeds This is found true in the case of samples tested at 14th and 21st days after treatment This confirms that the higher level of residues was present in the flesh of the fruits

5 7 Effect of storage on the degradation of carbofuran residues in cucumber fruits.

Results presented in Table 11 indicate that active metabolism and degradation of carbofuran residues in the fruit continue even when the fruits are harvested and kept under refrigeration for different periods The rate of degradation of total carbofuran was clearly shown in fig 4 The initial level of total carbofuran was 0 301 mg/kg which got reduced to 0 094 mg/kg by the 10th day of storage The percentage degradation on the 10th day was 68 8 percent from the initial level The rate of degradation was varying in different intervals

5 8 Waiting period of carbofuran in cucumber fruits when applied at the flowering stage of the crop

Results presented in Table 12 indicated that for safe consumption

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of fruits following carbofuran application at doses 0 5 ansd 1 5 kg ai/ha, a minimum waiting period of 25 and 26 days should be given

The results presented show that cucumber plants absorbed carbofuran rapidly from the soil and translocated the same to the leaves, vines and fruits resulting in peak residue levels w: 1-7 days after application and thereafter a declining trend observed

The metabolism of the compound was initiated on the first day itself in the plant system which is evidenced by the presence of metabolites namely 3-OH carbofuran and 3 keto carbofuran along with the parent compound pure carbofuran

Gas chromatographic studies revealed that residues of total carbofuran were observed maximum in the vines on the first day after treatment irrespective of the stages In the leaves and fruits maximum level of total carbofuran was observed on the 3rd and 7th day respectively for both the doses tested This shows that accumulation of carbofuran takes place first in the vines, followed by leaves and fruits

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Comparatively higher residues were detected in the vines leaves and fruits when applied at the higher dose (1 5 kg ai/ha) . The results also indicated that residues of pure carbofuran are much lower than those of total carbofuran in samples collected at 1,3,7,14,21 and 28th day after application The conversion of original carbofuran to less toxic metabolites commences as scon as the toxicant is absorbed into the plant and continues till it gets completely dissipated

In the present study the waiting period wi fixed taking into consideration the MRL of 0 2mg/kg fixed for grain crops Thus in the present study the results indicated that a waiting period of 25 and 26 days should be recommended for lower and higher dose respectively Since cucumber fruits are harvested at 20-30 days after the flowering of the crop the use of carbofuran granules at the flowering stage of the plant should be avoided to prevent the residue hazard

SUMMARY

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SUMMARY

The metabolism and persistence of carbofuran in cucumber plants when applied at 0 5 and 1 5 kg ai/ha at different growth stages of the crop viz sowing vining and flowering were studied in detail Samples of leaves vines and fruits were collected at intervals of 1 3 7 14 21 and 28 days after application of the insecticide and subjected to chemical analysis The contents of insecticide residues were determined in terms of total carbofuran pure carbofuran 3 OH carbofuran and 3 keto carbofuran using gas chromatographic technique

The results indicated that active absorption and metabolism of the compound was initiated on the first day after the application of the chemical as evidenced by the presence of 3 OH carbofuran and 3 keto carbofuran along with the parent compound pure carbofuran in all the samples tested The peak level of residues was detected in different occasions in the leaf vine and in the fruit samples Thus in the vines the highest level of total carbofuran pure carbofuran and the metabolites 3 OH carbofuran and 3 keto carbofuran were detected on the first day after the treatment the values being 0 761 0 203 0 309 and 0 249 mg/kg respectively for 0 5 kg ai/ha and 1 837 0 472 0 763 and 0 601 mg/kg respectively for 1 5kg ai/ha

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The highest level of total carbofuran was observed in the leaves on the third day after treatment and the levels being 0 995 and 1 248 mg/kg at sowing 0 890 and 2 641 mg/kg at vining and 0 494 and 0 934 mg/kg at flowering for 0 5 and 1 5 kg respectively But in the case of the fruit sample the highest level was reached on the seventh day after treatment the values being 0 921 and 1 238 mg/kg respectively for the lower and higher dose

A gradual decline in the residues was noticed thereafter from the peak level in the various portions The residues of parent compound and the metabolites were almost non detectable by the 28 DAT

The results clearly indicated that accumulation of total carbofuran takes place first in the vines followed by leaves and then in the fruits The conversion of carbofuran to different metabolites 3 OH carbofuran and 3 keto carbofuran commenced soon after the toxicant is absorbed into the plant system and continued till it gets completely dissipated Comparatively higher residues were detected in vines and fruits when applied at the higher dose (1 5 kg ai/ha)

The effect of peeling on the removal of total carbofuran residues was studied by estimating the residues in the peeled samples The result showed that peeling could reduce the level of total

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carbofuran residues considerably

The distribution of carbofuran residues in different portions of cucumber fruits top middle and basal when treated at the flowering stage of the crop was studied The metabolism was similar in all the three portions tested as evidenced by the presence of pure carbofuran and the metabolites 3 OH carbofuran and 3 keto carbofuran The highest level of total carbofuran was detected in the top portion (distal portion) followed by middle and basal portion (fig 2) This shows that distal portion of the fruit carried maximum residues following insecticide application

The comparison of residues in the flesh and placenta of cucumber fruits when treated at the flowering stage of the crop revealed that 3 OH carbofuran and 3 keto carbofuran and pure carbofuran were present in the flesh and placenta at all the intervals tested (7 14 and 21 DAT) The results also showed that accumulation of residues of carbofuran and its metabolites were more in the flesh portion of the fruit than in the placenta (innercore and Seeds)

Studies on the effect of different periods of storage on the degradation of carbofuran residues showed that metabolism and degradation of the compound continued even after the fruits are harvested

But the rate of de radation was not steady throughout the different intervals observed (0,1,4,5 7 and 10) When carbofuran was applied at the vining stage of the crop the residues would be normally below the MRL in the fruits at the time of harvest The results also revealed that for safe consumption a waiting period of 25 and 26 days should be recommended at doses 0 5 and 1 5 kg ai/ha respectively so as to reach below the MRL of 0 2 ppm Since cucumber fruits are harvestd at 20 - 30 days after the flowering of the crop, the use of carbofuran granules at the flowering stage of the plant should be avoided to prevent the residue hazard

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CHEMODYNAMICS OF CARBOFURAN IN CUCUMBER

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ABSTRACT

A field experiment was conducted to study the chemodynamics of carbofuran in cucumber plants when applied as granule in the soil The insecticide was applied at two doses of 0 5 and 1 5 kg ai/ha at three occasions viz sowing vining and flowering stage of the crop The residues of carbofuran and its metabolites were estimated from the vines leaves and fruits at different intervals after the insecticidal treatment using gas chromatographic technique Distribution of the residues in the various portions of fruit and the effect of different periods of storage on the degradation of residues were also studied in detail A safe waiting period was also arrived so as to avoid residue hazards in consumption of the fruits

The results indicated that absorption and metabolism of carbofuran in the plant begins soon after its application in the soil Pure carbofuran and the metabolites 3 OH carbofuran and 3 keto carbofuran were detected in the vines leaves and fruit samples at 1 3 7 14 21 and 28 days after treatment

When the different portions of the plant were analysed the highest level of residues was detected at different occasions Thus in the vines the peak level of residues was seen on the

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first day after treatment where as in the leaves and fruits it was on the third and seventh day respectively A gradual decline was noticed thereafter and the residues reached almost non detectable by 28th day after treatment in all parts of the plant

The effect of peeling on residues was studied in a separate experiment and the results indicated that peeling of fruits could reduce the residues considerably Distribution of carbofuran residues in different fruit portions was studied and the results indicated that maximum accumulation of the residues took place in the top portions of the fruit followed by middle and basal portions

Comparing the carbofuran residues in the flesh and placenta of cucumber fruits when treated at the flowering stage of the crop it was observed that maximum accumulation of residues of carbofuran took place in the flesh portion when compared with the placenta of the fruit (inner core and seeds)

Effect of storing the fruits on the degradation of carbofuran residues showed that metabolism and degradation of the chemical continued even after harvest during the process of storage

For safe consumption of fruits following carbofuran treatment at the flowering stage a waiting period of 25 and 26 days have to be given when applied @ 0 5 and 1 5 kg ai/ha respectively