Bull Environ Contam Toxicol (2010) 84:602–605
DOI 10.1007/s00128-010-9994-z

# Degradation Dynamics of Chlorfenapyr Residue in Chili, Cabbage and Soil

**Papia Ditya · S. P. Das · P. K. Sarkar · Anjan Bhattacharyya**

Received: 17 November 2009 / Accepted: 8 April 2010 / Published online: 22 April 2010


**Abstract** Chlorfenapyr is a pyrrole group of insecticide, [4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethyl-1*H*-pyrrole-3-carbonitrile]used as broad spectrum insecticide/acaricide to control whitefly, thrips, caterpillars, mites, leafminers, aphids, etc., chlorfenapyr 10% SC formulation was applied on chili and cabbage twice @ 75 and 100 g a.i./ha along with untreated control. Chlorfenapyr was dissipated in chili, cabbage and soil following the first-order kinetics (log $C/C_0 = -kt$). The half lives of chlorfenapyr in chili, cabbage and soil were varying from 2.93 to 2.96 days, 2.98 to 3.62 days and 4.06 to 4.36 days respectively, according to the application rate.

**Keywords** Chlorfenapyr · Chili · Cabbage · Residue

Pesticides, besides saving crop losses, increase crop productivity, reduce cost of production, improve quality and thus help in the farmers' income. The role and contribution of pesticides will be much more in the coming years, especially the country like India. The demands for food continue to grow steadily due to fast growth of population. One of the major disadvantages of pesticide use is that residue in foodstuff seldom exceed the Maximum Residue Limits (MRLs) set by the food authorities. For this reason, proper monitoring of pesticide residues is very important for reducing health hazard to consumers. Vegetables are the rich sources of micronutrients and vitamins. India is the second largest producer of cabbage after China. Chili is an essential pillar of the cuisines of India. Chlorfenapyr [4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethyl-1*H*-pyrrole-3-carbonitrile] was first developed by American Cynamide Company. It is a novel broad spectrum insecticide-miticide and actually a pro-insecticide (Lovell et al. 1990; Black et al. 1994), used on cotton and experimentally on corn, soybeans, vegetables, tree and vine crops and ornamentals to control whitefly, thrips, caterpillars, mites, leafminers, aphids, and Colorado potato beetle. It is a systemic and stomach insecticide and working as an "uncoupler" or inhibitor of oxidative phosphorylation, preventing the formation of the crucial energy molecule adenosine triphosphate (ATP). EPA (US final rule, Sept 26, 2003) has regulated the chlorfenapyr by fixing MRLs 1 mg $kg^{-1}$ in or on raw agricultural food commodities. It was first registered in India for use in October, 1997. A field trial was carried out (Satpathy et al. 2005) to test the efficacy of chlorfenapyr 10 SC @ 75 and 100 g ai/ha against diamondback moth (DBM) in cabbage and it showed significantly less infestation at both the test concentrations (100 and 75 g ai/ha) of chlorfenapyr. Chlorfenapyr @ 75 g a.i./ha provided optimum control of DBM, over endosulfan and *Bt*. A number of work had been done of chlorfenapyr residue on vegetables (WeiGuo et al. 2007; YanLing et al. 2007; Ou et al. 2006), but a very few in Indian climatic condition.

The objective of this present study was to find out the residues, kinetics and dissipation pattern of chlorfenapyr 10% SC formulation in cabbage, chili and there field soil after application.

P. Ditya · S. P. Das
Department of Chemistry, University of Kalyani, Kalyani, West Bengal 741235, India
e-mail: papia_130@yahoo.co.in

P. K. Sarkar
Department of Agricultural Entomology, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal 741252, India

A. Bhattacharyya (✉)
Pesticide Residue Laboratory, Department of Agricultural, Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal 741252, India
e-mail: anjan_84@rediffmail.com

## Materials and Methods

Pesticide standard of chlorfenapyr was purchased from PESTANAL (Sigma–Aldrich) and 10% chlorfenapyr suspension concentrate formulation was supplied by M/S. Crystal Phosphates India Pvt. Ltd, New Delhi. Ethyl acetate was used as a solvent; all other solvents and chemicals used were of analytical grade (Rankem, India).

CHEMITO-1100 Gas chromatograph equipped with electron capture detector (ECD) was used for residue analysis. A DB 1701(30 m × 0.53 mm i.d, 1.5 μm film thickness) megabore column was employed as the analytical column. The carrier gas flow was 10 mL $min^{-1}$ of high purity nitrogen. The make up gas to the detector was nitrogen at 30 mL $min^{-1}$. Injector and detector were held at 275 and 300°C, respectively, the oven temperature was 250°C.

Field trials were carried out in Kakdwip located at West Bengal, India. Chili plants were planted with a spacing of 0.5 × 0.5 m ($24 \times 10^3$ plants/ha). A random design (RBD) was used, with three replications for each test. Treatments were carried out during April–May, 2008 (Kakdwip); using a Knapsack sprayer. Chlorfenapyr 10% SC formulation was applied at two recommended doses 75 g a.i/ha i.e. $T_1$ and 100 g a.i/ha i.e. $T_2$. To study the dissipation pattern, chili and soil samples were collected randomly from each treated plot as well as from the control plot at 0 (2 h), 1, 3, 7, 10 and 15 days after insecticide application.

Cabbage plants were transplanted in field having area 4 × 5 m. Each plot contained around 45 plants. The growing plants were treated with the pesticides under investigation at the recommended doses after the formation of plant heads. For each treatment, three plots were used and the plots were distributed in a completely randomized design (RBD), two untreated ($T_3$) plots were sprayed water as control. Chlorfenapyr 10% SC formulation was sprayed at recommended dose 75 g a.i/ha ($T_1$) and 1.33 times of the recommended dose 100 g a.i./ha ($T_2$) with Knapsack sprayer. Cabbage and soil samples were collected randomly from each plot after 0 (1 h after spraying), 1, 3, 7, 10 and 15 days of spraying. Sample for the untreated control ($T_3$) was collected in the similar way.

To avoid degradation in presence of light, all samples were collected and extracted as early as possible after collection. If not possible, they were stored in deep freeze at −18°C for a minimum period of time. The extracts were cleaned up immediately after application as far as possible but in some cases they were also stored in the refrigerator (−18°C) for a minimum period of time before analysis.

For the extraction of chlorfenapyr residue 100 mL of acetone was added to 20 g of chili sample. Then the mixture was shaken for about 1 h and it was filtered through Buchner funnel and washed with (30 + 30) mL acetone using an aspirator. The combined filtrate was concentrated in a rotary vacuum at 40°C. The sample extract was transferred to a separatory funnel containing 50 mL of 10% sodium chloride, and then followed by liquid–liquid partitioning with dichloromethane for three times (50 + 50 + 50) mL. Combined dichloromethane fraction was concentrated to 2 mL. The concentrated extract was transferred into a chromatographic glass column which was prepacked with 2 g sodium sulfate in the bottom, silica gel (5.0 g) in the middle, mixture of activated charcoal (0.3 g) and sodium sulfate (1.2 g) on the top and hexane as the packing solvent. The column was washed for 7 times (20 mL for each) with 99:1 hexane:toluene mixture. The total elute was collected and evaporated to dryness and then adjusted to a final volume of 10 ml with ethyl acetate and residue analysis was done in GC.

Extraction procedure of chlorfenapyr for cabbage sample was as follows, 20 g of cabbage sample was placed in a 250 mL conical flask and 100 mL of acetonitrile was added to it and soaked for over night. Then the mixture was shaken for about 1 h and it was filtered through Buchner funnel and washed with (30 + 30) mL acetone using an aspirator. The combined filtrate was concentrated in a rotary vacuum at 35°C. The sample extract was transferred to a separatory funnel containing 50 mL of 4% sodium chloride, and then followed by liquid–liquid partitioning with dichloromethane for three times at the volume of (50 + 50 + 50) mL. Combined dichloromethane fraction was concentrated to 2 mL. The concentrated extract was transferred into a chromatographic glass column which was packed with 2 g sodium sulfate in the bottom, silica gel in the middle, mixture of activated charcoal (0.25 g) and sodium sulfate (1.0 g) on the top and hexane as the packing solvent. The column was washed for 10 times (15 mL for each) with 99:1 hexane: toluene mixture. The total elute was collected and evaporated to dryness. Final volume was made up to 10 ml with ethyl acetate and residue of chlorfenapyr was determined by GC.

Cropped soil samples (50 g) were socked with 200 mL mixture of acetone and water 80:20 (v/v) for overnight. Then it was shaken for 1 h in a mechanical shaker and filtered through a Buchner funnel using 50 mL of acetone as washing solvent. The combined extracts were evaporated with a rotary vacuum evaporator, at 40°C until the final volume reached to 20 mL. Then the sample was transferred to a separatory funnel containing 100 mL of 4% sodium chloride, and then followed by liquid–liquid partitioning with dichloromethane for three times at the volume of 50, 30 and 30 mL, respectively. The concentrated sample was dissolved in ethyl acetate to a volume 10 mL before GC analysis.

To determine the reliability of the above analytical method, recovery studies were carried out by fortifying control chili, cabbage and soil sample with 0.01, 0.05 and 0.25, and 0.50 and 1.00 mg $kg^{-1}$ standard of chlorfenapyr separately. Recoveries were found in the range of 89%–92.3% in chili, 91%–96% in cabbage and 90%–97% in soil. Four replicates for each concentration were analyzed.

Dissipation data was subjected to regression equation (Hoskins 1961) for computing residual half-life.

## Results and Discussion

Standard calibration curve of chlorfenapyr was constructed by plotting concentrations against peak areas. Good linearity was achieved in the range of 0.01–2.0 mg/kg.

Limit of detection (LOD) and limit of quantification (LOQ) were considered when a signal to noise ratio (S/N) of 3:1 and 10:1, respectively (3). In this study LOD and LOQ were considered as 0.01 and 0.05 $mgkg^{-1}$, respectively.

Initial deposits, dissipation percent, half-life values and regression equation of chlorfenapyr in chili, cabbage and soil are presented in Tables 1, 2, 3, and 4. The results showed that the residues of chlorfenapyr in chili, cabbage and soil decreased progressively with time irrespective of application rates. The residue level decreased to below detectable limit on the 15th, 10th and 15th in chili, cabbage and soil samples irrespective of any doses. In the untreated control ($T_3$), chlorfenapyr residues were not detected. The half-life values calculated from the best-fit lines of the logarithm of residual concentrations versus time period, suggested first order reaction kinetics in the dissipation of chlorfenapyr residue. The study revealed that the dissipation rate was independent of initial deposit. As evident from the analytical data Table 1 average initial deposit on 0(2 h) day of chlorfenapyr residues in chili samples were found to be 0.81 and 1.40 mg/kg for $T_1$ and $T_2$ respectively which were dissipated to 0.07 and 0.14 mg/kg in 10 days after application. In 15 days after application the residues were below detectable limit for both the treatments. The percentages of dissipation recorded on 10th days were 93% and 90%, respectively. The average initial deposit in soil was 0.183 and 0.289 mg/kg on 0(1 h) days for $T_1$ and $T_2$, respectively. No residues were found for both treatments in 15 days after application. It was dissipated up to 82.51% and 82.35% in 10 days for $T_1$ and $T_2$, respectively. Table 2 describes the kinetic data of chlorfenapyr dissipation in chili and soil. The dissipation of chlorfenapyr in chili and cropped soil followed the first-order kinetics with the half-life values varying from 2.98 to 2.96 days and 4.04 to 4.06 days, respectively according to the application rate.

As evident from the analytical data Table 3 average initial deposits on 0(2 h) day of chlorfenapyr residues in cabbage samples were found to be 1.02 mg/kg and 1.90 mg/kg for $T_1$ and $T_2$, respectively which were dissipated to 0.19 and 0.48 mg/kg in 7 days after application. In 10 days after application the residues were reached to below detectable limit for both the treatments. The

**Table 1** Residues of chlorfenapyr in chili and soil

| Date of sampling (Days) | $T_1$ (75 g a.i./ha) | | $T_2$ (100 g a.i./ha) | |
|---|---|---|---|---|
| | Chili<br>Mean ± SD (mg/kg)<br>Dissipation (%) | Soil<br>Mean ± SD (mg/kg)<br>Dissipation (%) | Chili<br>Mean ± SD (mg/kg)<br>Dissipation (%) | Soil<br>Mean ± SD (mg/kg)<br>Dissipation (%) |
| 0 | 0.81 ± 0.08 | 0.183 ± 0.032 | 1.40 ± 0.05 | 0.289 ± 0.068 |
| 1 | 0.63 ± 0.02 (22) | 0.142 ± 0.026 (22.4) | 1.00 ± 0.07 (28) | 0.230 ± 0.049 (20.41) |
| 3 | 0.43 ± 0.03 (47) | 0.093 ± 0.024 (49.18) | 0.83 ± 0.03 (41) | 0.155 ± 0.043 (46.36) |
| 7 | 0.16 ± 0.02 (80) | 0.050 ± 0.020 (72.67) | 0.25 ± 0.02 (83) | 0.083 ± 0.026 (71.28) |
| 10 | 0.07 ± 0.01 (93) | 0.032 ± 0.029 (82.51) | 0.14 ± 0.01 (90) | 0.051 ± 0.024 (82.35) |
| 15 | BDL | BDL | BDL | BDL |

* Average of three replicate; BDL means below detectable limit

**Table 2** Dissipation kinetic equation of chlorfenapyr in chili and soil

| Kinetic parameters | $T_1$ (75 g a.i./ha) | | $T_2$ (100 g a.i./ha) | |
|---|---|---|---|---|
| | Chili | Soil | Chili | Soil |
| Half-life ($t_{1/2}$) (Days) | 2.93 | 4.04 | 2.96 | 4.06 |
| Regression equation | $y = 2.85–0.102x$ | $y = 2.22–0.0744x$ | $y = 3.13–0.101x$ | $y = 2.439–0.0741x$ |
| $R^2$ | 0.9822 | 0. 9924 | 0.9751 | 0. 9967 |

**Table 3** Residues of chlorfenapyr in cabbage and soil

| Date of sampling (Days) | $T_1$ (75 g a.i./ha) | | $T_2$ (100 g a.i./ha) | |
|---|---|---|---|---|
| | Cabbage Mean ± SD (mg/kg) Dissipation (%) | Soil Mean ± SD (mg/kg) Dissipation (%) | Cabbage Mean ± SD (mg/kg) Dissipation (%) | Soil Mean ± SD (mg/kg) Dissipation (%) |
| 0 | 1.02 ± 0.02 | 0.985 ± 0.04 | 1.90 ± 0.10 | 1.64 ± 0.11 |
| 1 | 0.76 ± 0.03 (25.49) | 0.720 ± 0.02 (26.90) | 1.48 ± 0.09 (22.10) | 1.44 ± 0.04 (12.19) |
| 3 | 0.64 ± 0.05 (37.25) | 0.520 ± 0.04 (47.20) | 1.11 ± 0.13 (41.57) | 1.12 ± 0.02 (31.70) |
| 7 | 0.19 ± 0.06 (81.37) | 0.300 ± 0.01 (69.54) | 0.48 ± 0.05 (74.73) | 0.60 ± 0.11 (56.09) |
| 10 | BDL (100) | 0.163 ± 0.04 (83.45) | BDL (100) | 0.35 ± 0.01 (78.65) |

* Average of three replicate; BDL means below detectable limit

**Table 4** Dissipation kinetic equation of chlorfenapyr in cabbage and soil

| Kinetic parameters | $T_1$ (75 g a.i./ha) | | $T_2$ (100 g a.i./ha) | |
|---|---|---|---|---|
| | Cabbage | Soil | Cabbage | Soil |
| Half-life ($t_{1/2}$) (Days) | 2.98 | 4.06 | 3.62 | 4.36 |
| Regression equation | $y = 3.02–0.101x$ | $y = 2.960–0.073x$ | $y = 3.274–0.083x$ | $y = 3.233–0.069x$ |
| $R^2$ | 0.965 | 0.990 | 0.995 | 0.993 |

percentages of dissipation recorded on 10th days were 81.37% and 74.73%, respectively. The average initial deposit in soil was 0.985 mg/kg and 1.64 mg/kg on 0(1 h) days for $T_1$ and $T_2$, respectively. No residues were found for both treatment in15 days after application. It was dissipated up to 83.45% and 78.65% in 10 days for $T_1$ and $T_2$, respectively. Table 4 describes the kinetic data of chlorfenapyr dissipation in cabbage and soil. The dissipation of chlorfenapyr in cabbage and cropped soil followed the first-order kinetics with the half-life values varying from 2.98 to 3.62 days and 4.06 to 4.36 days, respectively irrespective of any doses.

Chlorfenapyr 10% SC formulation became undetectable after 15 days in all substrates.

**Acknowledgments** This work was supported financially by M/S. Crystal Phosphates India Pvt. Ltd, New Delhi.

## References

Black BC, Hollingworth RM, Ahammadsahib KI, Kukel CD, Donovan S (1994) Insecticidal action and mitochondrial uncoupling activity of AC-303630 and related halogenated pyrroles. Pestic Biochem Physiol 50:115–128

Hoskins WM (1961) Mathematical treatment of the rate of loss of pesticide residues. FAO Pl Prot Bull 9:163–168

Lovell JB, Wright DP, Gard IE, Miller TP, Treacy MF, Addor RW et al. (1990) AC303630—an insecticide/acaricide from a novel class of chemistry. In: Proceedings of the Brighton crop protection conference, British crop protection council on pests and diseases, vol 1, Brighton, UK7 Thornton Heath, pp 43–48

Ou XM, Huang MZ, Wang XG, Fan D (2006) Dissipation of chlorfenapyr residue in pakchoi and soil. Bull Environ Contam Toxicol 77(6):810–815

Satpathy S, Kumar A, Singh AK, Pandey PK (2005) Chlorfenapyr: a new molecule for diamondback moth (Plutella xylostella L.) management in cabbage. Ann Plant Prot Sci 13(1)

WeiGuo HFU, Guo C, Ting Y (2007) Residue detection of chlorfenapyr in vegetables. Acta-Agriculturae-Zhejiangensis 19(2): 119–122

YanLing MAI, HongMei LIU, ChengLan LIU, WenTuan C, MeiYing H (2007) Study on residue dynamics of chlorfenapyr in cucumber and amaranth. J South China Agric Univ 28(1):67–69