Bull Environ Contam Toxicol (2012) 89:322–327
DOI 10.1007/s00128-012-0691-y

Degradation Dynamics of Chromafenozide in Different Types of Soil

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Received: 21 February 2012 / Accepted: 18 May 2012 / Published online: 10 June 2012

Abstract Chromafenozide is a lepidopteran insecticide. It is highly effective in controlling various lepidopteran pests. Chromafenozide technical and formulation (80WP) was applied at 2.5 and 5.0 μg g^{-1} in 4 types of soils (air dried and sieved) separately in laboratory condition. Half-lives of active ingredient were calculated and found at 15.8, 21.6, 25 and 23.9 days for single dose for chromafenozide technical (99.4 %).

Keywords Chromafenozide · HPLC · Residue · Formulation · Soil

Several hundred pesticides of different chemical structures are used worldwide in agriculture for saving crop losses and increasing crop productivity. The main problem linked to over use of pesticide is the contamination of soil and water sources including the aquatic system. Several scientists reported effect of pesticides in soil (Frampton et al. 2006; Coupe et al. 2005; Willian and Mueller 1994; Balasubramanya and Patil 1980). Integrated pest management (IPM) programs were introduced in order to minimize sole dependence on chemical control of pests because of undesirable side effects on the environment. Such effects include the health hazards of human on account of exposure to traces of these toxicants, which may have no acute effect, but chronic exposure may result in serious health hazards. Generally, IPM programs have not been practically developed for most of the crops in India. Once the pollutants enter into the environment, it may persist and enter into food chain by bioaccumulation. It is known that the fate and degradation of environmental chemicals are largely affected by interactions with humic substances widespread in water, soil and environmental system. Soil pH has an influence on the rate of dissipation of the pesticide (Sabadie 1990). Some researchers reported damage to rotation or substitution crops due to soil residue of pesticides (Moyer et al. 1990; Schneiders et al. 1993; Yutai et al. 1999).

Chromafenozide, a dibenzoyl group of insecticide is going to be introduced by M/S PII Industries Ltd. in India. Chromafenozide (2′-tert-butyl-5-methyl-2′-(3,5-xyloyl)-chromane-6-carbohydrazide) is an ecdysone receptor agonist or moulting accelerating compound (MAC), which is non-steroidal ecdysone analog and mimics the natural function of the endogenous moulting hormone 20-hydroxy-ecdysone (Fig. 1).

It was discovered and developed under cooperative works by Nippon Kayaku Co., Ltd. and Sankyo Co., Ltd. Chromafenozide is one of the most suitable plant protection products for the IPM to which growing attention is being attracted with recent global needs for sustainable agriculture.

The present study has been designed to investigate the effect of different rates of dissipation of chromafenozide applied to four types of soil samples viz. acid soil (pH 5.45) from Jhargram, neutral soil (pH 7.02) from Mohanpur, saline soil (pH 7.6) from canning and black soil (pH 8.14) from Nasik. The soil samples were studied under laboratory condition. The degradation of chromafenozide was studied with technical standard (99.4 %) and formulation

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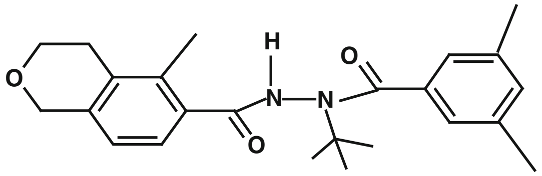

Fig. 1 Chromafenozide

(wettable powder) in a laboratory simulated condition. Formulation was selected in order to further evaluate the effect on the persistence-behavior of the compound.

Materials and Methods

Chromafenozide technical standard (99.4 %) was supplied by Nippon Kayaku Co. Ltd., Japan. Chromafenozide 80WP formulation was supplied by M/s PI Industries Ltd., Gurgaon. Water was distilled and filtered through Milli-Q apparatus (Millipore, USA). Acetonitrile solvent was of HPLC grade (E.Merck, India). Other solvents, used for extraction were distilled prior to use. Florisil of 60–100 mesh was purchased from Spectrochem (India). Other reagents were used of Analytical-Grade (SRL, India))Stock standard solutions of the active ingredient were prepared in acetonitrile.

Laboratory trial was carried out in Pesticide Residue Laboratory, Directorate of Research Building, B.C.K.V., Kalyani, India. The soil samples used in the experiment correspond to the following areas (1) Jhargram (acid soil) (2) Mohanpur (neutral soil) (3) Canning (saline soil) (4) Nasik (black soil). Soil samples from the upper layer were air dried and sieved (<0.63 mm). The physico-chemical properties of the soils were analyzed and shown in Table 1. The experiment was carried out during May–August, 2007. The temperature and the relative humidity inside the laboratory were 24–37°C and 62 %–96 %, respectively. Chromafenozide technical and formulation were applied at two recommended doses 2.5 µg/g of soil i.e. T_1 and 5.0 µg/g of soil i.e. T_2 and untreated control i.e. T_3. After application of chromafenozide technical and formulation separately to the soil samples of different pH (5.45, 7.02, 7.60 and 8.14), chromafenozide was extracted from the same at 0 (2 h), 1, 3, 7, 15, 30, 60 and 90 days interval to study the dissipation pattern. Control soil samples were also extracted in the same day for every types of soil.

Chromafenozide was analyzed using a SHIMADZU-LC-10AT HPLC system equipped with Photodiode Array Detector (PDA). A Phenomenex-Luna 5 μ reverse phase (RPC_{18}) column (4.6 × 250 mm) was employed. The mobile phase of acetonitrile: water (7:3) was used to determine the chromafenozide. The flow rate was 1 mL min^{-1}. The injection volume and wavelength were 20 µL and 224 nm, respectively.

Soil was crushed in a hammer mill and sieved to obtain same size granules; 50 g soil was socked overnight in a 250 mL conical flask with a mixture of water and acetonitrile 20:80 (v/v) of 100 mL. Subsequently, the extracts were shaken for 1 h on a mechanical shaker and filtered through Whatman no. 1 filter paper. Filtrates were evaporated with rotary vacuum evaporator at 40°C. The concentrate obtained, was transferred to separating funnel containing 50 mL of 5 % sodium chloride, followed by liquid–liquid partitioning with dichloromethane for three times at the volume of 40, 30 and 30 mL, respectively. Organic layer was collected, concentrated and then dissolved about in 5 mL of hexane and transferred to a chromatographic column (300 × 30 mm (id)), packed with florisil which was washed with 5 mL of hexane prior to use. The column was washed with 20 mL hexane/ethyl acetate (17:3, v/v) and the elute was discarded. Chromafenozide was eluted from the column with 50 mL of dichloromethane. The extract was evaporated to dryness and transferred quantitatively with acetonitrile to a 10 mL volumetric flask to be used for injection in the HPLC.

To determine the reliability of the above analytical method, recovery studies were carried out by fortifying control soil samples of different types with 0.03, 0.1 and 1.0 mg kg^{-1} standard of chromafenozide separately. Recoveries were found 89.00 %, 94.66 %, 94.00 % and 95.53 % in acidic soil, neutral soil, saline soil and black soil, respectively. Three replicates for each concentration were analyzed and three injections were made for each replication.

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

Results and Discussion

Standard calibration curve of chromafenozide was constructed by plotting concentrations against peak areas. Good linearity was achieved in the range of 0.03–10.0 mg kg^{-1} with $R^2 = 1.0$.

LOD and LOQ of chromafenozide are 0.01 and 0.03 mg kg^{-1} in soil.

The average percentages of recovery were recorded 89 %, 94.66 %, 94 % and 95.53 % for acid, neutral, saline and black soil, respectively. Hence the analytical method was quite satisfactory and adopted for the residue and dissipation study for the corresponding substrate.

The mean residue values, dissipation percentage, regression equation and half lives of chromafenozide technical and formulation in four different types of soil are presented in Tables 2, 3, 4 and 5. From the table it revealed that

Table 1 Soil properties

Location	pH	Texture	Bulk density (g/cm^3)	Organic carbon (%)
Jhargram	5.45	Clay loam	1.58	0.48
Mohanpur	7.02	Silty clay loam	1.28	0.88
Canning	7.60	Sandy clay loam	1.45	1.02
Nasik	8.14	Clayey	1.60	0.67

Table 2 Dissipation of chromafenozide technical in different soils

Date of sampling (days)	T_1				T_2			
	Acidic soil Mean[a] ± SD (mg kg^{-1}) Dissipation (%)	Neutral soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Saline soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Black soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Acidic soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Neutral soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Saline soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Black soil Mean ± SD (mg kg^{-1}) Dissipation (%)
0	0.93 ± 0.025	0.85 ± 0.05	1.03 ± 0.03	0.85 ± 0.02	1.81 ± 0.09	1.63 ± 0.30	1.94 ± 0.12	1.77 ± 0.06
1	0.85 ± 0.03 (6)	0.67 ± 0.08 (21)	1.02 ± 0.07 (1)	0.65 ± 0.01 (24)	1.50 ± 0.2 (15)	1.28 ± 0.03 (21)	1.81 ± 0.10 (6.7)	1.34 ± 0.05 (32)
3	0.71 ± 0.015 (12)	0.54 ± 0.02 (36)	0.89 ± 0.09 (11)	0.54 ± 0.03 (36)	1.14 ± 0.05 (37)	1.00 ± 0.10 (38)	1.67 ± 0.08 (14)	1.13 ± 0.08 (36)
7	0.55 ± 0.04 (41)	0.43 ± 0.06 (49)	0.67 ± 0.04 (33)	0.46 ± 0.02 (46)	0.91 ± 0.09 (50)	0.86 ± 0.08 (47)	1.33 ± 0.15 (31)	0.95 ± 0.05 (46)
15	0.37 ± 0.026 (60)	0.40 ± 0.03 (53)	0.52 ± 0.10 (48)	0.36 ± 0.03 (58)	0.64 ± 0.02 (65)	0.65 ± 0.04 (60)	1.07 ± 0.20 (45)	0.62 ± 0.02 (65)
30	0.22 ± 0.020 (77)	0.25 ± 0.03 (71)	0.29 ± 0.05 (71)	0.27 ± 0.0 (68)	0.46 ± 0.06 (75)	0.49 ± 0.02 (70)	0.75 ± 0.1 (61)	0.41 ± 0.0 (77)
60	0.22 ± 0.020 (77)	0.10 ± 0.019 (88)	0.15 ± 0.05 (85)	0.12 ± 0.0 (86)	0.12 ± 0.04 (96)	0.20 ± 0.02 (88)	0.30 ± 0.05 (86)	0.24 ± 0.0 (86)
90	BDL[b]	BDL	0.08 ± 0.02 (92)	BDL	BDL	0.06 ± 0.03 (96)	0.17 ± 0.04 (91)	0.11 ± 0.03 (93)

[a] Mean = average of three replications for each treatment and three injections of each replication

[b] BDL means below detectable limit

chromafenozide technical and formulation dissipated linearly with increment of time and it follows first order kinetics. As expected, no residue of chromafenozide was obtained in the untreated control samples throughout the study.

Figure 2 shows the residue of chromafenozide in acid soil (pH 5.45) over the testing time period. Initial deposits of chromafenozide technical in acidic soil were in the range of 0.87–1.81 μg g^{-1} for irrespective of treated dosage. Chromafenozide WP formulation showed the same level of initial deposit on acidic soil with chromafenozide technical. A gradual and continuous deterioration of the pesticide residues in and on the treated acid soil was observed as a function of time after application. The half-life of chromafenozide technical in acidic soil was varying from 15.84 to 16.72 days and for chromafenozide WP formulation, it was varying from 15.92 to 20.00 days. More than 75 % of initial deposits were dissipated within 30 days after application; it became undetectable after 90 days of application. From residual data in Tables 2, 3, 4 and 5, a sharp decline of residues occurred for chromafenozide technical; a comparatively slow rate of degradation was noticed for wettable powder formulation.

As evident from the analytical data Tables 2 and 4, average initial deposits of chromafenozide residues on 0 (2 h) day, in neutral soil (pH 7.02) samples were found in the range of 0.88–0.85 μg g^{-1} for T_1 and 1.63–1.77 μg g^{-1} for T_2 and the same were dissipated to 0.10–0.13 and 0.20–0.41 μg g^{-1} respectively after 60 days of application. More than 95 % of initial deposits were dissipated within 90 days after application for both chromafenozide technical and formulation. For T_2, the percentages of dissipation recorded on 60th day were 88 % and 77 % for chromafenozide technical and formulation (WP) respectively in neutral soil. Tables 3 and 5 describe the kinetic data of chromafenozide technical and WP formulation in soils. The half-life values varying from 21.65 to 22.13 days for technical grade and 22.63 to 25.50 days for chromafenozide WP formulation. Figure 3 shows the residue of chromafenozide in neutral soil over the testing time period. In case of neutral soil, a comparatively slow rate of dissipation was observed

Table 3 Dissipation kinetic equation of chromafenozide technical in soils

Kinetic parameters	T_1				T_2			
	Acidic soil	Neutral soil	Saline soil	Black soil	Acidic soil	Neutral soil	Saline soil	Black soil
Half-life (days)	15.84	21.65	25.00	23.88	16.72	22.13	25.5	24.67
Regression equation	$y = 2.915 - 0.019x$	$y = 2.8196 - 0.0139x$	$y = 2.951 - 0.012x$	$y = 2.809 - 0.0126x$	$y = 3.155 - 0.018x$	$y = 3.09 - 0.0136x$	$y = 3.241 - 0.011x$	$y = 3.093 - 0.012x$
R^2	0.9725	0.9607	0.9725	0.9489	0.9891	0.9493	0.9891	0.9524

Table 4 Dissipation of chromafenozide formulation (80WP) in different soils

Date of sampling (days)	T_1				T_2			
	Acidic soil Mean[a] ± SD (mg kg^{-1}) Dissipation (%)	Neutral soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Saline soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Black soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Acidic soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Neutral soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Saline soil Mean ± SD (mg kg^{-1}) Dissipation (%)	Black soil Mean ± SD (mg kg^{-1}) Dissipation (%)
0	0.87 ± 0.03	0.88 ± 0.51	1.04 ± 0.05	0.84 ± 0.02	1.74 ± 0.12	1.77 ± 0.20	1.8 ± 0.08	1.77 ± 0.06
1	0.73 ± 0.039 (12)	0.78 ± 0.02 (11)	0.88 ± 0.02 (15)	0.64 ± 0.03 (24)	1.37 ± 0.15 (21)	1.47 ± 0.15 (17)	1.6 ± 0.06 (11)	1.37 ± 0.0 (23)
3	0.63 ± 0.02 (28)	0.66 ± 0.15 (25)	0.73 ± 0.0 (29)	0.58 ± 0.0 (31)	1.13 ± 0.15 (35)	1.25 ± 0.15 (39)	1.4 ± 0.15 (22)	1.14 ± 0.0 (36)
7	0.55 ± 0.03 (37)	0.58 ± 0.01 (34)	0.61 ± 0.0 (39)	0.44 ± 0.04 (47)	0.93 ± 0.02 (47)	0.95 ± 0.047 (46)	1.1 ± 0.14 (39)	0.95 ± 0.0 (46)
15	0.38 ± 0.05 (44)	0.41 ± 0.01 (55)	0.50 ± 0.0 (50)	0.32 ± 0.0 (62)	0.61 ± 0.02 (65)	0.70 ± 0.015 (61)	0.88 ± 0.1 (51)	0.64 ± 0.03 (64)
30	0.18 ± 0.03 (79)	0.27 ± 0.02 (69)	0.3 ± 0.10 (70)	0.25 ± 0.0 (70)	0.46 ± 0.04 (74)	0.57 ± 0.38 (69)	0.64 ± 0.2 (64)	0.42 ± 0.0 (76)
60	0.06 ± 0.01 (93)	0.13 ± 0.01 (85)	0.20 ± 0.0 (80)	0.12 ± 0.04 (86)	0.18 ± 0.02 (90)	0.41 ± 0.047 (77)	0.38 ± 0.2 (79)	0.32 ± 0.0 (82)
90	BDL[b]	BDL	BDL	BDL	BDL	0.10 ± 0.036 (95)	0.08 ± 0.0 (96)	0.07 ± 0.0 (96)

[a] Mean = average of three replications for each treatment and three injections of each replication

[b] BDL means below detectable limit

for wettable powder formulation in respect to the chromafenozide technical standard.

Figure 4 shows the residue of chromafenozide in saline soil over the testing time period. Initial deposits of chromafenozide technical in saline soil were in the range of 1.03–1.94 µg g^{-1} irrespective of treated doses. Chromafenozide WP formulation showed the same level of initial deposit on saline soil with chromafenozide technical. A gradual and continuous deterioration of the pesticide residues in the treated saline soil was observed as a function of time after application. The half-life of chromafenozide technical in saline soil was varying from 25 to 25.5 days and for chromafenozide WP formulation, it was varying from 26.6 to 28.1 days. More than 90 % of initial deposits were dissipated within 90 days after application; it became undetectable after 90 days of application. From residual data in Tables 2, 3, 4 and 5, a sharp decline of residues occurred for chromafenozide technical; a comparatively slow rate of degradation was noticed for wettable powder formulation.

Figure 5 shows the residue of chromafenozide in black soil (8.14) over the testing time period. Initial deposits of chromafenozide technical in black soil were in the range of 0.84–1.77 µg g^{-1} irrespective of treated doses. Chromafenozide WP formulation showed the same level of initial deposit on black soil with chromafenozide technical. Above 75 % of initial deposits were dissipated within 30 days after application for both chromafenozide technical and formulation. For T_2, the percentages of dissipation recorded on 90th days were 93 % and 96 % for chromafenozide technical and formulation (WP) respectively in alkaline soil. Tables 3 and 5 describe the kinetic data of chromafenozide technical and WP formulation in soils. The half-life values varying from 23.88 to 24.67 days for

Table 5 Dissipation kinetic equation of chromafenozide 80WP in soils

Kinetic parameters	T_1				T_2			
	Acidic soil	Neutral soil	Saline soil	Black soil	Acidic soil	Neutral soil	Saline soil	Black soil
Half-life (days)	15.9	22.6	26.6	23.7	20.0	25.5	28.1	24.3
Regression equation	$y = 2.8782 - 0.0189x$	$y = 2.875 - 0.013x$	$y = 2.914 - 0.011x$	$y = 2.799 - 0.012x$	$y = 3.1211 - 0.015x$	$y = 2.875 - 0.013x$	$y = 3.174 - 0.010x$	$y = 3.107 - 0.012x$
R^2	0.922	0.974	0.922	0.9327	0.9433	0.9374	0.943	0.9422

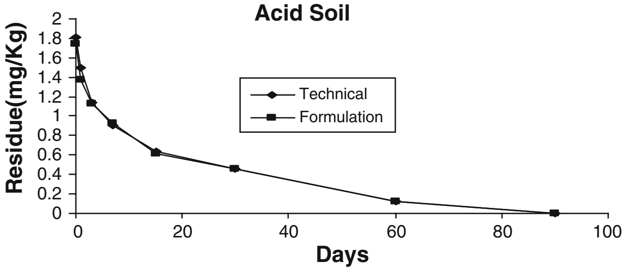

Fig. 2 The degradation curves of chromafenozide in acid soil

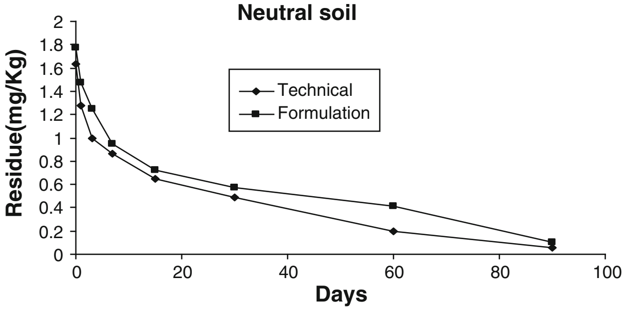

Fig. 3 The degradation curves of chromafenozide in neutral soil

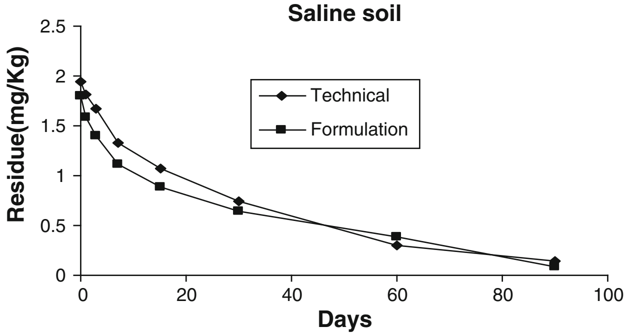

Fig. 4 The degradation curves of chromafenozide in saline soil

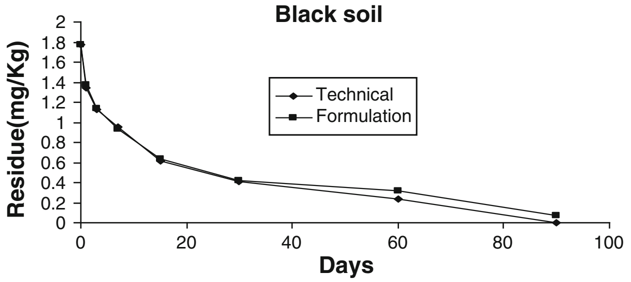

Fig. 5 The degradation curves of chromafenozide in black soil

technical grade and 23.7 to 24.3 days for chromafenozide WP formulation. In case of alkaline soil, same rate of dissipation was observed for chromafenozide technical grade and its wettable powder formulation.

In laboratory condition, the initial concentration of the residues were found to varying from 0.85 to 1.03 µg g^{-1} for T_1 and 1.63 to 1.94 µg g^{-1} for T_2 in case of chromafenozide technical and for formulation it varying from 0.84 to 1.04 µg g^{-1} for T_1 and 1.74 to 1.8 µg g^{-1} for T_2 irrespective of soil type. After the 90 days of experimental condition the remaining residue was found in the range of 0.0–0.08 µg g^{-1} and 0.06–0.17 µg g^{-1} for technical grade and for formulation 0.00 µg g^{-1} and 0.00–0.08 µg g^{-1}, respectively for recommended dose and double the recommended dose irrespective of soil types. Stability of chromafenozide is lowest at acidic soil (pH 5.45). Very few references are found for chromafenozide dissipation study. The field dissipation ($DT_{50)}$ of chromafenozide in paddy soils found in the range of 22–136 days (Tomlin 2009) which is in agreement with the half lives found from this study.

Therefore, from the results it revealed that chromafenozide dissipated rapidly in acidic soil than in other tested soils. The rate of dissipation of chromafenozide was decreased in the order of acidic soil > neutral soil > black soil > saline soil. Same trend of degradation was observed in chromafenozide technical and WP formulation. But comparatively slower rate of degradation was noticed for wettable powder formulation than chromafenozide technical in soils. This slow rate of dissipation could be attributed to inhibition of formulating reagent. It was also observed from the results that 91 %–100 % of initial concentration was dissipated at 90 days of experimental condition.

Considering this dissipation of chromafenozide at the tested doses in soils under laboratory condition, it's much faster degradation can be expected under field condition.

Acknowledgments This work was supported by the Residue Analysis Laboratory, B.C.K.V, Mohanpur, India. We are grateful to PI Industries Ltd., Goregaon, India for there kind cooperation for the experiment.

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