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Assessing the dissipation behavior of bifenthrin in coarse textured soils under laboratory conditions

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Abstract
Bifenthrin was applied at two different doses (recommended and double the recommended dose) to study its kinetics and dissipation behavior in coarse textured soils like sandy loam and sandy soils under laboratory conditions. Samples were collected at regular time intervals after application and analyzed by gas chromatography equipped with electron capture detector. From the results of the study, it was found that bifenthrin residues applied at double dose persisted for more than 50 days in both the soils. Dissipation of the bifenthrin was very rapidly, which led to less persistence of the insecticides at single dose. The soils showed monophasic and biphasic mode of bifenthrin dissipation in sandy loam and sandy soils, respectively. Higher dissipation of bifenthrin in coarse-textured soils like sandy loam and sandy soils than fine textured soils is due to less adsorption on the soil surface.

Keywords: bifenthrin, kinetics, dissipation, QuEChERS, coarse textured soils

Introduction

Different pesticides are used in soil and water to effectively control insects and pests and thus maintain agricultural production. Though there has been a manifold increase in crop yields, the indiscriminate and intensive use of these chemicals has led to the contamination of different environmental components (Lund and Narahashi, 1981) [7]. Besides agriculture, pesticides are also used for public health applications to control mosquitoes, houseflies, cockroaches etc. (Tewary *et al.*, 2005) [16]. When any pesticide is applied to different crops as a foliar application, only little amount of the pesticide reaches the target and a majority of the compound makes its way to different environmental compartments. The soil acts as a sink for different pesticides and the toxic nature of these chemicals leads to the deterioration of soil health. Soil is a heterogeneous mixture of the inorganic and organic components with a porous structure, which can strongly bind these compounds at low concentration (Pinto *et al.*, 2011) [13].

Bifenthrin (2-methyl-3-phenylbenzyl(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2 dimthylcyclopropanecarboxylate) is a third-generation pesticide belonging to pyrethroid family (Tewary *et al.*, 2005; Meena *et al*, 2021) [16]. It is an insecticide as well as acaricide which is used both in agriculture to control aphids, white fly, colorado beetle in various crops and public health application against mosquitoes, houseflies, cockroaches etc (Lee *et al.*, 2004) [6]. Bifenthrin has low potential to volatilize into air when applied to dry soil. As the pesticide has lower water solubility, it has correspondingly strong tendency to bind to soil and thus found in runoff sediments (Gan *et al.*, 2005) [4]. Soil contaminated with bifenthrin can increase the toxic concentration in water bodies. Due to the good soil bonding capacity of bifenthrin, the compound is tightly adsorbed on soil particle hence its bioavailability decreases (Rashid *et al.*, 2020) [14]. The variation in the soil properties can lead to different behavior of the compound under laboratory and field conditions. Though different studies have been carried out to assess the effect of moisture (Manoj and Gajbhiye, 2008) [8], microbial community (Sharma and Singh, 2012) [15] on dissipation of bifenthrin in soil under laboratory conditions but very little information is available on the dissipation behavior of the pesticide in different kinds of soil. This type of study can help to assess the behavior of the pesticide in different soils so as to utilize the efficiency of the chemical well in the field conditions at different geographical locations. Therefore a laboratory experiment was conducted to study the dissipation behavior and kinetics of bifenthrin in different types of soil.

Material and Methods

Soils

A laboratory experiment was conducted at All India Network Project on Pesticide Residues, Indian Council of Agricultural Research (ICAR) Unit- 9, Anand Agricultural University (AAU), Anand, Gujarat to study the kinetics and dissipation behavior of bifenthrin in sandy loam and sandy soil collected from Anand Agricultural University and Sardarkrushinagar Dantiwada Agricultural University, Gujarat India, respectively, were used in this experiment. The soils had no history of bifenthrin application in any of the four places. The remains of stubbles, macro fauna, stones and other debris were removed from the soils followed by air drying at the ambient temperature. The soils were then sieved through 2 mm sieve, homogenized carefully and stored in dry condition at room temperature. Soils were spiked and further used for residue analysis of bifenthrin.

Chemicals used

The certified reference materials (CRM) of bifenthrin (98.58% purity) were procured from Sigma Aldrich India Limited.

Physico-chemical properties

The purified bifenthrin is melting at 68-70 °C, with a fatty odour under normal temperature and pressure conditions. It decomposes before boiling at 285 °C. Its relative density is 1.316 g cm^{-3}. It is almost insoluble (< 1 µg L^{-1}) in water at 20°C at all tested pH's (Meena *et al.*, 2021). Bifenthrin is not flammable, and has a flash point higher than 110 °C. It does not present explosive or oxidizing properties. It is stable in storage conditions for up to 2 years. The chemical structure of bifenthrin is shown in Figure 1.

Chemical formula	$C_{23}H_{22}ClF_3O_2$
CAS No.	82657-04-3
Molecular mass (g/mol)	422.9 g mol^{-1}
Vapour pressure (mmHg) at 25 ºC	1.8×10^{-7}
Octonal water coefficient (K_{ow})	1.0×10^{6}
Henry constant atm. (m^3/mol)	7.20×10^{-3}

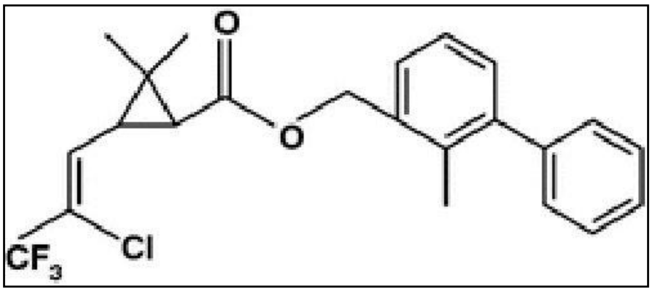

Fig 1: Chemical structure of bifenthrin

The working standards of bifenthrin were prepared at concentrations of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1.0 µg $mL^{-1}$from the primary standard solution (100 µg mL^{-1}), which was prepared in petroleum spirit.

Soils (10 g) were spiked with bifenthrin analytical standard solution (100 µg mL^{-1}) at two doses: single dose 0.06 µg g^{-1} (T_2) and double dose 0.12 µg g^{-1} (T_3) that were kept at room temperature. Moisture content was maintained at field capacity level. The experiment was replicated thrice along with control (T_1). These spiked soil samples collected at regular time intervals (0, 1, 3, 5, 7, 10, 20, 30, 40, 50 and 60 d) were analyzed for bifenthrin residue.

Extraction and clean up

Extraction and clean-up was carried out as per method of Caldas *et al.* (2011) [2] with minor modification. A representative 10 g soil was taken into a 50 mL centrifuge tube and then add 20 mL acetonitrile after that mixture of 4 g $MgSO_4$ + 1 g NaCl, shaken vigorously by hand (1 min.) before centrifugation. Thereafter tubes were centrifuged at 3500 rpm for 3 minutes. A 10 mL aliquot was taken into 15 mL centrifuge tubes that contain 1.5 g $MgSO_4$ and 0.25 g PSA (Primary Secondary Amine), by auto pipette subsequently centrifugation at 2500 rpm for 2 minutes. A 4 mL aliquot was transferred into glass test tube and completely evaporated on Turbo Vap® LV. Final volume was made to 2 mL in petroleum spirit: acetone (1:1 v/v) and residues were quantified on Gas Chromatography (GC) equipped with electron capture detector (ECD).

Instrumentation

Bifenthrin residues were quantified on Varian 450 GC equipped with TG-5-Sil MS (30 m × 0.25 mm × 0.25 µm) column and ^{63}Ni ECD. The column temperature was maintained from 160 ºC (2 min.), increased to 280 ºC, that was for 10 min. The injector and detector temperatures were 250 and 295 ºC, respectively. The carrier gas flow in the column was 1.5 mL/ min and make up gas flow was 30 mL/min. The total run time was 10 min.

Calculation and statistical analysis

The simple statistical analysis was carried out in the Microsoft Excel- 2010 program with the help of computer. The residues of bifenthrin were quantified with following equation:

$$\text{Bifenthrin concentration (mg/kg)} = \frac{A1}{A2} \times \frac{V}{W} \times C$$

Where, A_1 = Peak area/height of sample (mV), A_2 = Peak area/height of standard (mV), V = Volume of sample extract (mL), W = Weight of sample used for extraction (g) and C = Concentration of bifenthrin (µg/mL) in standard solution.

The half- lives of pesticides were also calculated by using the following equation:

$$t\,½ = \frac{ln\ (0.5)}{k}$$

Where, t ½ = half-life of bifenthrin, days and k = dissipation rate constant, $days^{-1}$

Results and Discussion

Average recovery percentages of soils at three spiking levels (0.05, 0.25 and 0.50 µg/g) were in the range of 86.75- 119.03 and 96.27- 118.30 %, and per cent RSD were in the range of 9.56- 15.58 and 5.28- 6.30 % for sandy loam and sandy soils, respectively. Control samples were free of bifenthrin residues (Table 1). As per SANTE guidelines[16], all recoveries were above 85 per cent and RSD_{WR} below 20% is accurate and precise. LOQ of bifenthrin was 0.01 µg g^{-1}. Similarly, bifenthrin recovery in sandy loam soil varied from 92.6 to 93.8 percent at 0.5 and 1.0 µg/g levels of fortification, while the LOQ of bifenthrin was 0.01 µg g^{-1}(Sharma and Singh, 2012) [15]. Bhuva, (2015) [1] also reported that per cent recovery of bifenthrin was in the range 86- 117 % in clay, sandy loam and sandy soil. According to Meyer *et al.* (2013)

[10], the typical recoveries of pyrethroid test mixtures were between 74 and 106 percent. The gas chromatogram of bifenthrin in sandy loam and sandy soils are depicted in Figure 2.

Table 1: Recovery of bifenthrin in sandy loam and sandy soils

Soil type	Fortification level (µg/g)	Mean Recovery (%) *n** = 5	Standard Deviation (±SD)	% RSD
Sandy loam	0.05	96.68	13.42	13.88
	0.25	86.75	13.52	15.58
	0.50	119.03	11.38	9.56
Sandy	0.05	105.19	5.56	5.28
	0.25	96.27	6.75	7.01
	0.50	118.30	7.45	6.30

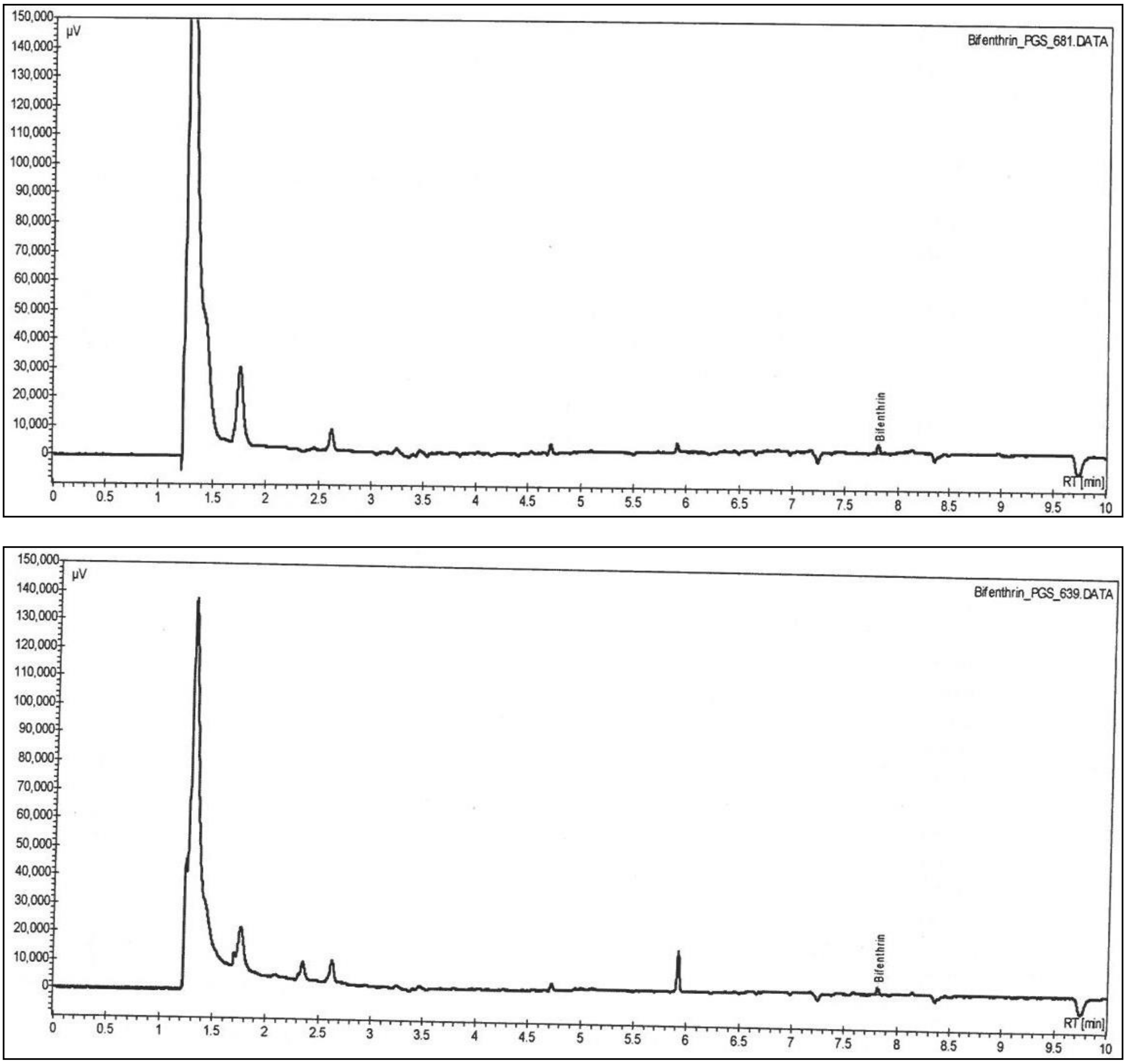

Fig 2: The chromatogram of bifenthrin in a) Sandy loam and b) Sandy soil at 0.06 µg g^{-1}

In sandy loam soil, on 0 day (one hour after treatment), bifenthrin residues were found to be 0.032 and 0.079 µg g^{-1} at single and double dose, respectively. Within 24 hours, the corresponding level showed 21.88 and 22.78 per cent loss at single and double dose, respectively (Table 2). At single dose the residue dissipated with half- life of 11.1 days, whereas for the double dose, half- life was 27.4 days. At both doses, the mode of dissipation was monophasic (Figure 3).

Table 2: Residue and dissipation pattern of bifenthrin in sandy loam soil

Days after treatment	Residue (µg g^{-1})				
	Dose				
	T_1 (Control)	T_2 (0.06 µg g^{-1})		T_3(0.12 µg g^{-1})	
		Mean(±SD) (n = 3)	% loss over initial	Mean(±SD) (n = 3)	% loss over initial
0	ND	0.032 (±0.001)	-	0.079 (±0.002)	-
1	ND	0.025 (±0.000)	21.88	0.061 (±0.016)	22.78
3	ND	0.020 (±0.000)	37.50	0.056 (±0.003)	29.11
5	ND	0.018 (±0.002)	43.75	0.048 (±0.004)	39.24
7	ND	0.017 (±0.002)	46.88	0.046 (±0.001)	41.77
10	ND	0.016 (±0.001)	50.00	0.043 (±0.003)	45.57
20	ND	0.016 (±0.002)	50.00	0.034 (±0.002)	56.96
30	ND	0.010 (±0.001)	71.88	0.020 (±0.003)	74.68
40	ND	<LOQ	-	0.019 (±0.002)	75.94
50	ND	<LOQ	-	0.015 (±0.001)	81.01
60	ND	<LOQ	-	0.012 (±0.001)	84.81
Regression equation R^2		Y = -0.027X + 1.435 R^2 = 0.825 (0-10 day) T-Half = 11.1 days		Y= -0.011X + 1.756 R^2 = 0.975 (0-60 day) T-Half = 27.4 days	

LOQ- Limit of Quantification = 0.01 µg g^{-1}

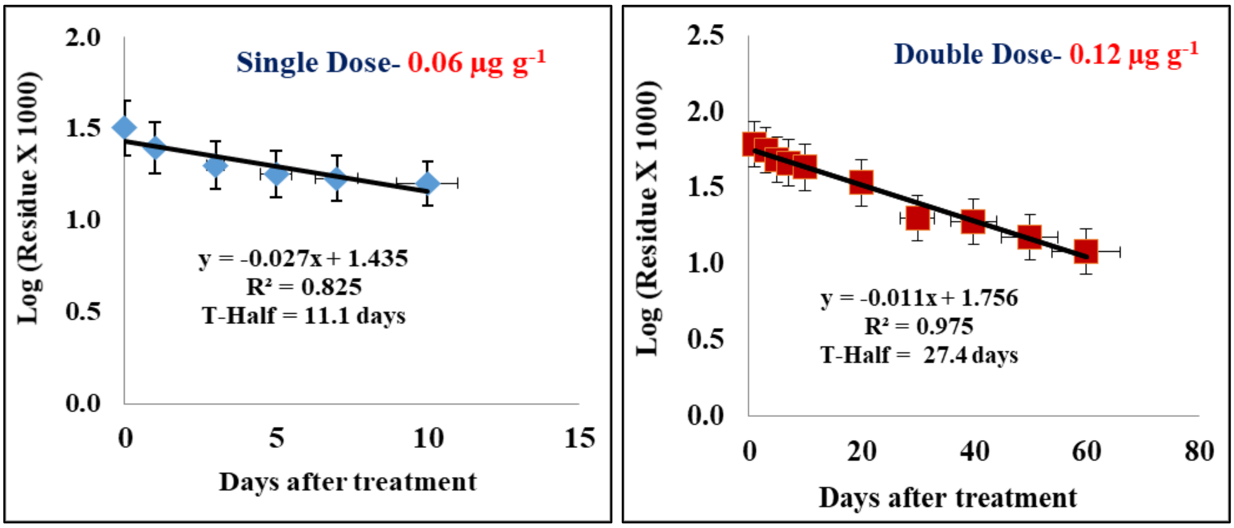

Fig 3: Dissipation pattern of bifenthrin at single and double dose in sandy loam soil

The dissipation of bifenthrin in sandy soil was biphasic in nature at both the doses (Figure 4). Initially (one hour after treatment), bifenthrin residues were found to be 0.037 and 0.049 µg g^{-1} which declined to 0.029 and 0.036 µg g^{-1} within 24 hours at single and double dose, respectively (Table 3). At single dose, the half- life values were 4.6 and 25 days during phase- I (0- 5 days) and phase- II (5- 20 days), respectively. At the double dose, half- life values were 12.4 and 75.3 days during phase- I (0- 10 days) and phase- II (10- 60 days), respectively.

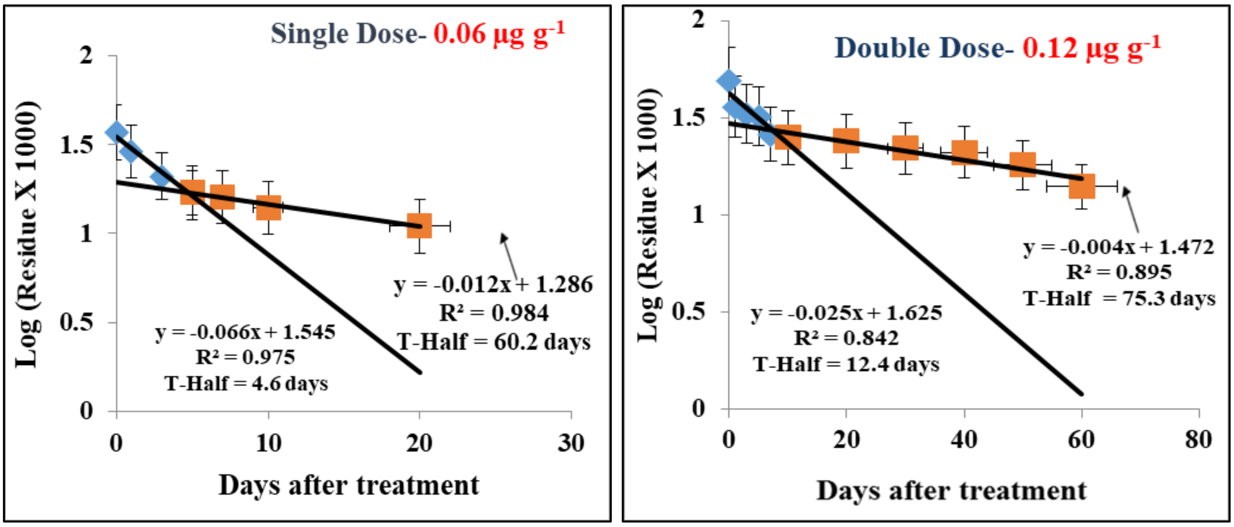

Fig 4: Dissipation pattern of bifenthrin at single and double dose in sandy soil

Table 3: Residue and dissipation pattern of bifenthrin in sandy soil

Days after treatment	Residue ($\mu g\ g^{-1}$)				
	Dose				
	T_1 (Control)	T_2 (0.06 $\mu g\ g^{-1}$)		T_3(0.12 $\mu g\ g^{-1}$)	
		Mean (±SD) (*n* = 3)	% loss over initial	Mean (±SD) (*n* = 3)	% loss over initial
0	ND	0.037 (±0.003)	-	0.049 (±0.003)	-
1	ND	0.029 (±0.004)	21.62	0.036 (±0.007)	26.53
3	ND	0.021 (±0.001)	43.24	0.033 (±0.001)	32.65
5	ND	0.017 (±0.001)	54.05	0.032 (±0.001)	34.69
7	ND	0.016 (±0.001)	56.76	0.026 (±0.001)	46.94
10	ND	0.014 (±0.000)	62.16	0.025 (±0.001)	48.98
20	ND	0.011 (±0.001)	70.27	0.024 (±0.002)	51.02
30	ND	0.010 (±0.001)	75.68	0.022 (±0.004)	55.10
40	ND	<LOQ	-	0.021 (±0.002)	57.14
50	ND	<LOQ	-	0.018 (±0.001)	63.26
60	ND	<LOQ	-	0.014 (±0.001)	71.42
Regression equation R^2	Phase- I	Y = -0.066X + 1.545 R^2 = 0.975 (0-5 days) T-Half = 4.6 days		Y= -0.025X + 1.625 R^2 = 0.842 (0-10 days) T-Half = 12.4 days	
	Phase- II	Y = -0.012X + 1.286 R^2 = 0.984 (5- 20 days) T-Half = 25 days		Y = -0.004X + 1.472 R^2 = 0.895 (10- 60 days) T-Half = 75.3 days	

From the results of the study, it was found that bifenthrin residues applied at double dose persisted for more than 50 days in both the soils. Similarly, the residues of fipronil in soil were below detectable levels after 47 days of the spray applied and the half life of fipronil in soil was found to be 7.3 days (Pei *et al.*, 2004) [12].

The study revealed pesticide applied at higher dose showed erratic pattern and longer persistence in soils as compared to the lower dose. In both the soils, initially maximum dissipation of bifenthrin was observed in sandy loam followed by in sandy soil. The residues of bifenthrin dissipated almost 85 % in 15 days in sandy soil (Kumari, 2012) [5]. The soils showed monophasic and biphasic mode of bifenthrin dissipation in sandy loam and sandy soils, respectively. Higher dissipation of bifenthrin in coarse-textured soils like sandy loam and sandy soils than fine textured soils is due to less adsorption on the soil surface. Similar results have also been reported for pyraclonil, which showed higher adsorption affinity to clay minerals and low mobility into the soil (Zhang *et al.*, 2020; Ou *et al.*, 2020) [17, 11]. Pesticide breakdown rate was influenced by the mechanical component of the pesticide. Organic soil has a higher persistence for pyrethroid insecticides than inorganic soil (Chapman and Harris, 1981) [3]. Bifenthrin residues in clay, sandy loam, and sandy soils were found up to 30 days and half-life was 21.2 days (Bhuva, 2015) [1]. The sterile and non-sterile soils had half-life values of 330 and 147 days, respectively. The large variation in half-life values between the two soils indicated that microbial degradation had a significant role in bifenthrin dissipation (Sharma and Singh 2012) [15]. Manzoor and Pervez (2017) [9] reported that bifenthrin levels in sandy loam and sandy clay loam soils were steady under three years of application.

Conclusions

The results of the present investigation demonstrated that application of bifenthrin at their recommended dose resulted in dissipation of the residues was very rapidly, which led to less persistence of the insecticides. Bifenthrin residues persisted for more than 50 days in both the soils at double dose. The soils showed monophasic and biphasic mode of bifenthrin dissipation in sandy loam and sandy soils, respectively. Higher dissipation of bifenthrin in coarse-textured soils like sandy loam and sandy soils than fine textured soils is due to less adsorption on the soil surface.

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