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Dissipation of β-Cyfluthrin in Water as Affected by Sediment, pH, and Temperature

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β-Cyfluthrin ((α-cyano-(4-fluoro-3-phenoxyphenyl)-methyl-3-(2,2-dichloroethen-yl)-2,2-dimethyl cyclopropanecarboxylate), a non-systemic synthetic pyrethroid insecticide, is highly effective against a variety of insect pests of agricultural crops (Dikshit and Singh 2000; Sinha and Gopal 2002; Berg and Rensberg 1993). The compound is also being used against pests of public health importance such as mosquitoes, houseflies and cockroaches (Zhuang 1996; Yap et al. 1997; Braness and Bennett 1992). It exhibits larvicidal activity against *Aedes aegypti*, *Armigeres subalbatus* and oviposition deterrent activity against *Culex quinquefasciatus* (Vasuki and Rajavel 1992). The efficacy of β-cyfluthrin impregnated fabrics, curtains and bed nets have also been evaluated extensively (Ansari and Razdan 2000; Curtis et al. 1996; Zaim et al. 1998). Following its application in human habitats to control pests, the insecticide may leave its harmful residues on various surfaces. The residues may also find its way into surface water bodies due to direct application or washing of treated surfaces. Even though reports are available on its bioefficacy following application on various types of surfaces like soil, wood, steel, glass, etc. (Kaufman and Rutz 2000; Ladonni 1998; Arthur 1994), very little information is available on its persistence in water. The residues may be subjected to varied pH and temperature depending on climatic conditions. Therefore, present investigation was undertaken to study the dissipation of β-cyfluthrin from water as affected by pH, temperature and sediments.

MATERIALS AND METHODS

Analytical grade β-cyfluthrin (purity 99%) and its formulation Bulldock 025 SC (2.5% active ingredient) were supplied by M/s Bayer India Ltd. Stock solution of analytical grade β-cyfluthrin (~1000 $\mu g\ ml^{-1}$) was prepared in acetone and diluted with *n*-hexane to obtain working standards. For treatment of water, the formulation (Bulldock 025 SC) was diluted with distilled water to get various concentrations. All the chemicals/reagents/solvents were of analytical grade purity and were procured from S.D. Fine Chemicals and Qualigens Fine Chemicals. Acetone, hexane and dichloromethane were glass distilled before use.

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All the dissipation studies were carried out under laboratory conditions. For studying the dissipation in water, 20 ml water was taken in test tubes and fortified at 0.01 and 0.1 μg ml^{-1} level with pesticide formulation. The tubes were kept in BOD incubator at 25 ± 1°C and samples were drawn at periodic intervals.

The effect of sediment was studied by applying pesticide formulation in conditioned water soil-sediment system. Water (18 ml/tube) was taken in 50 ml capacity graduated ground glass joint tubes. In each tube 1 g air-dried and sieved soil collected from Indian Agricultural Research Institute's research farms was added and left undisturbed for settling down the soil. After 48 hours, ~ 1 ml diluted solutions of formulation were added to the tubes to get fortification level of 1.0 and 0.1 μg ml^{-1} on 20 ml water basis. Diluted formulation and additional water was added very carefully from the top so as not to disturb the water-sediment system. The treated samples were kept in BOD incubator at 25 ± 1°C. On each sampling day three replicates from each treatment were drawn. Tubes were centrifuged at 2000 rpm for 10 minutes and 17 ml supernatant withdrawn with the help of pipette. Withdrawn supernatant and sediment along with remaining 3 ml solution were processed separately.

The effect of pH was studied by treating the buffered water of pH 4.0, 7.0 and 9.2 with formulation of β-cyfluthrin. The buffer solutions were prepared by dissolving buffer tablets (Qualigen make) in distilled water (one buffer tablet/100 ml water). The buffer solutions of different pH were mixed with diluted formulation to get the fortification level of 1.0 μg ml^{-1}. Treated solutions were kept in BOD incubator at 25 ± 1°C. On each sampling day, 20 ml sample aliquot, in triplicate, were drawn from each flask and processed.

To study effect of temperature, water was treated with diluted formulation to get the fortification level of 1.0 and 0.1 μg ml^{-1} and 20 ml aliquots were transferred into 50 ml capacity graduated ground glass joint tubes. The tubes were divided into three sets. One set was kept in refrigerator maintained at 5 ± 1°C, second set kept at 40 ± 1°C in incubating oven and third set placed in BOD incubator at 25 ± 1°C. Water lost from the tubes was maintained by replenishing it on every alternate day. On different sampling days three tubes per treatment per temperature were taken out and processed.

Aqueous samples from different experiments were diluted with ~20 ml NaCl solution (10%) and extracted thrice with dichloromethane using 30 ml fresh solvent each time. Combined dichloromethane extract was passed through anhydrous Na_2SO_4 and concentrated using Kuderna-Danish evaporator.

Sediment (1 g) along with 3 ml solution was extracted with acetone by dipping and decanting method. Process of extraction was repeated three times using 30 ml fresh acetone each time. Combined extract was filtered through Whatman filter paper and concentrated to 5 ml. The concentrated extract was diluted with NaCl solution and extracted with dichloromethane as in case of aqueous samples.

Residues obtained from different experiments were dissolved in *n*-hexane for quantitative analysis. The estimation of β-cyfluthrin was done by gas liquid chromatography (GLC) using Hewlett Packard 5890 series II instrument equipped with ^{63}Ni electron capture detector (ECD), auto injector (7673), mega bore HP-1 column (10 m x 0.53 mm id, 2.65 μm film thickness). The operating temperatures (°C) were : detector 300, injector 280, oven 250 for 10 min. The carrier gas was high purity nitrogen (IOLAR I grade) with flow rate of 15 ml min^{-1}. Under these conditions the retention time of β-cyfluthrin was 3.08 minutes.

The recoveries of β-cyfluthrin from untreated water and wet soil samples (sediments) were determined by fortifying the samples in triplicate and analyzing them. Water sample (250 ml) was fortified at 0.01 and 0.1 μg ml^{-1} level and the sediment (20 g air-dry) was fortified at 0.1 and 1.0 μg g^{-1} level by adding standard solution of β-cyfluthrin. Fortified samples of water and sediments were processed as described above.

Half-lives were calculated based on first order dissipation kinetics ($C = C_o e^{-Kt}$, where C = concentration after time t, C_o = apparent initial concentration and K = rate constant). Single compartment or two compartment model as applicable was followed.

RESULTS AND DISCUSSION

The recoveries of β-cyfluthrin from water samples fortified at 0.01 and 0.1 μg ml^{-1} varied from 92-97 %. Similarly, the recoveries from wet soil samples (sediments) fortified at 0.1 and 1.0 μg ml^{-1} level varied from 87-90 %. The limits of determination for the reported methods were 0.001 μg ml^{-1} for water and 0.005 μg g^{-1} for sediment samples.

The dissipation of β-cyfluthrin from water was studied at two concentration levels 0.1 and 0.01 μg ml^{-1} at 25 °C temperature. The initial deposits of 0.1 and 0.01 μg ml^{-1} in water dissipated with time and 90-100 % dissipation was recorded on 30th day (Table 1). The dissipation followed first order kinetics (one compartment model) with half-life of 8.4-10.5 days. Though no reports are available on persistence of cyfluthrin in water, the studies on other synthetic pyrethroids like permethrin, cypermethrin and fenvalerate showed that they persisted for 15 days in water with initial deposits ranging from 0.04-0.09 μg ml^{-1} level (Agnihotri et al. 1989).

The effect of sediment on dissipation of β-cyfluthrin was studied at two concentration levels i.e. 0.1 and 1.0 μg ml^{-1}. The dissipation from water in water-sediment system followed two-compartment model with very fast dissipation during initial period of 5 days as compared to simple water system (Figure 1). For the first five days, the half-life of β-cyfluthrin in water varied from 0.75-0.81 days in water in water sediment system as compared to 8.4-10.5 days in simple water system.

Table 1. Persistence of β-cyfluthrin following application of pesticide formulation to water alone (without sediment) and water + sediment system. Experiment carried out at ambient temperature (25 ± 1°C).

Days	Residues (mean of three replicates)							
	Water without sediment		Water with sediment					
	0.01	0.1	0.1			1.0		
	Water (μg ml^{-1})	Water (μg ml^{-1})	Water (μg ml^{-1})	Sediment (μg g^{-1})	Total Amount (μg)	Water (μg ml^{-1})	Sediment (μg g^{-1})	Total Amount (μg)
0	0.0099	0.096	0.089	-	1.78 (0)	0.882 (0)	-	17.64 (0)
1	0.0094 (5.0)[a]	0.091 (5.2)	-	-	-	-	-	-
3	0.0085 (14.1)	0.088 (8.3)	0.0044 (95.0)	0.739	0.827 (53.5)	0.022 (97.5)	9.174	9.614 (45.5)
5	0.0071 (28.3)	0.080 (16.7)	0.0013 (98.5)	0.539	0.565 (68.2)	0.010 (98.8)	7.86	8.066 (54.3)
10	0.0053 (46.5)	0.041 (57.3)	BDL (100)	0.170	0.170 (90.4)	0.0036 (99.6)	5.406	5.478 (68.9)
15	0.0037 (62.6)	0.021 (78.1)	BDL	0.139	0.139 (92.2)	0.0029 (99.7)	3.704	3.762 (78.7)
20	-[b]	-		0.097	0.097 (94.6)	0.0019 (99.8)	2.797	2.836 (83.9)
30	BDL[c] (100)	0.010 (89.6)		0.064	0.064 (96.4)	0.0015 (99.9)	1.889	1.920 (89.1)

[a] Figures in parentheses denotes % dissipation
[b] Samples not drawn
[c] Below detectable limit (< 0.001μg ml^{-1})

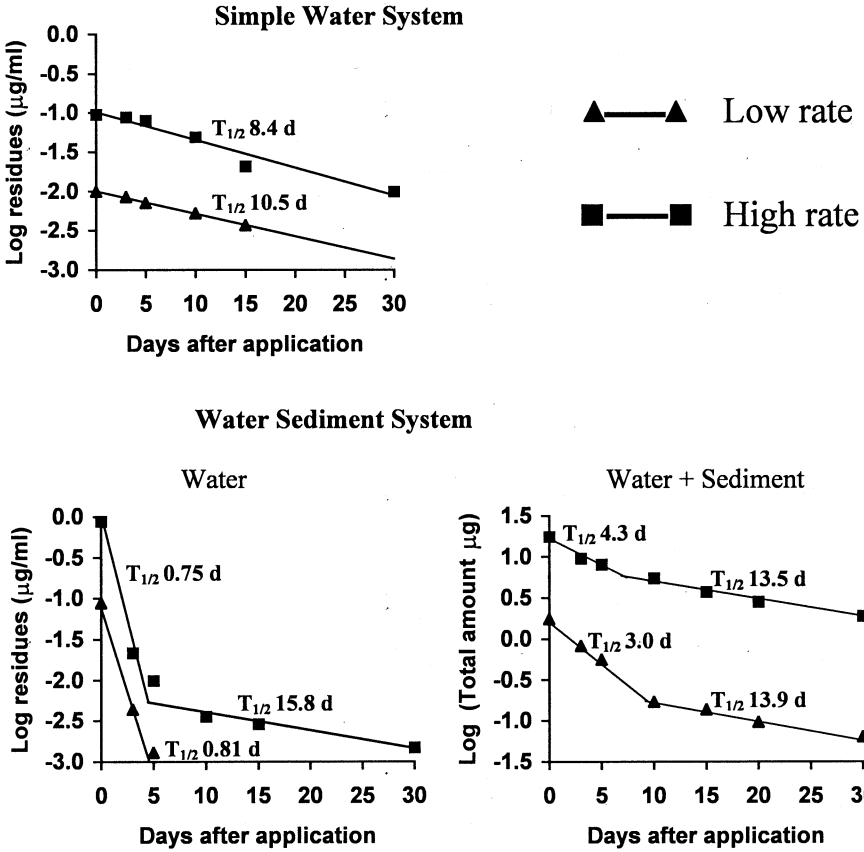

Figure 1. First order dissipation of β-cyfluthrin in water and water sediment system

The initial faster dissipation of residues from water in water sediment system could be attributed to its adsorption on sediment and volatilization from the water surface. A high value of octanol-water partition coefficient (K_{OW}) ranging from 4.58×10^5 - 6.4×10^5 suggests a strong tendency of β-cyfluthrin to partition from water to soil. On 3rd day, of the total amount present in the system, 4-10 % was present in water whereas major amount 90-96 % was present in sediment. However, the dissipation from sediment was slower and residues were recorded up to 30 days (Table 1). It seems that adsorbed residues desorbed and maintained some concentration in the supernatant water. Even though the concentration in water was low, the residues were detected up to 30 days at high rate of treatment. Dissipation of total amount (water + sediment) in water sediment system also followed two compartment model of first order dissipation with fast dissipation during initial period. Half-life values for the first five days varied from 3.0-4.3 days as compared to 13.5-13.9 days during 10-30 days period (Figure 1). The initial fast dissipation could be attributed to high volatilization from water surface

Table 2. Effect of pH on the dissipation of β-cyfluthrin at 25±1 °C following treatment of buffered water with pesticide formulation @ 0.1μg ml^{-1} .

Days	Residues (μg ml^{-1}) (mean of three replicates)		
	pH 4	pH 7	pH 9
0	0.1	0.1	0.1
2	0.1 (0)[a]	0.093 (7)	0.075 (25.5)
4	0.097 (3)	0.087 (13)	0.060 (40)
7	0.096 (4)	0.084 (16)	0.048 (52)
10	0.094 (6)	0.080 (20)	0.043 (57)
15	0.092 (8)	0.061 (39)	0.038 (62)
30	0.085 (15)	0.042 (58)	0.016 (84.1)
$T_{1/2}$ (days)	125.4	23.9	13.4

[a] Figures in parentheses denotes % dissipation

that decreased with time as residues got adsorbed on the sediment. Similar observation of initial fast dissipation and overall longer persistence in water sediment system has also been reported by Agnihotri et al. (1989) for other synthetic pyrethroids and organophosphorus insecticides.

β-Cyfluthrin dissipation in water was studied at three pH values i.e. 4.0, 7.0 and 9.2 using 0.1 μg ml^{-1} fortification level. The residue data is presented in Table 2. The residues persisted beyond 30 days in all the treatment. About 15-84 % residues dissipated in 30 days. The dissipation followed first order kinetics with half-life ranging from 13-125 days (Table 2). The dissipation was slightly slower in buffer solution of pH 7 than the natural water probably due to the use of distilled water for preparation of buffer solutions, which had least microbial activity.

The dissipation of β-cyfluthrin was fastest at pH 9 followed by pH 7 and pH 4. At pH 4.0, degradation was extremely slow and only 15 % dissipation was recorded on 30th day. It seems that β-cyfluthrin is highly stable under acidic pH. Shehata et al. (1987) have also reported that pH of soil had a significant effect on the degradation of cyfluthrin and an increase of pH from 5 to 9.18 accelerated the breakdown. Similarly, β-cyfluthrin is reported to have a hydrolysis half-lives of 117, 20 and 6 days at pH 4, 7 and 9, respectively (Anonymous 1994).

The effect of temperature on dissipation of β-cyfluthrin was studied at two concentration levels i.e. 0.1 and 0.01 μg ml^{-1} and three different temperatures regimes *viz* 5 ± 1 °C, 25 ± 1 °C and at 40 ± 1 °C. Residue data is presented in Table 3. As expected, β-cyfluthrin persisted longer at lower temperature than at higher temperatures at both the concentration levels (Table 3). Overall dissipation on 15th days was 90-92 % at 40 °C as compared to 62-78 % at 25 °C and 47-61 % at 5 °C. Similar effect of temperature on dissipation has been reported for other synthetic pyrethroids (Watters et al. 1983), heptachlor (Shivankar and Kavadia1989) and endosulfan (Kaur et al. 1998).

Table 3. Dissipation of β-cyfluthrin in water stored at different temperatures after treatment with pesticide formulation.

Days	Residues (μg ml^{-1}) (mean of three replicates)					
	5 °C		25 °C		40 °C	
	0.1	0.01	0.1	0.01	0.1	0.01
0	0.096	0.0099	0.096	0.0099	0.096	0.0099
1	0.094 (2.1)[a]	0.009 (9.1)	0.091 (5.2)	0.0094 (5.0)	0.064 (43.7)	0.0089 (10.1)
3	0.0767 (20.1)	0.0083 (16.2)	0.088 (8.3)	0.0085 (14.1)	0.049 (59.4)	0.0079 (20.2)
5	0.0747 (22.2)	0.0076 (23.2)	0.08 (16.7)	0.0071 (28.3)	0.036 (62.5)	0.0063 (36.4)
10	0.058 (52.0)	0.0058 (41.4)	0.041 (57.3)	0.0053 (46.5)	0.024 (75.0)	0.0036 (63.6)
15	0.0476 (60.8)	0.0053 (46.5)	0.021 (78.1)	0.0037 (62.6)	0.0072 (92.5)	0.001 (89.9)
$T_{1/2}$ (days)	15.1	16.4	8.5	10.5	5.8	4.7

[a] Figures in parentheses denotes % dissipation

The present study has shown that β-cyfluthrin residues persist in water up to 15 days with half-life of 8-10 days. The presence of sediment increased the loss of pesticide from water by adsorption during initial period. The pesticide in sediment dissipated very slowly, thereby increasing the overall persistence in water-sediment system. β-Cyfluthrin was found to be highly stable under acidic condition and dissipation increased with increase in pH. β-Cyfluthrin dissipated faster at higher temperature than the lower. It is expected that β-cyfluthrin will persist longer in water with acidic pH and cold temperatures.

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