Bull. Environ. Contam. Toxicol. (2001) 66:9–16

DOI: 10.1007/s001280000198

Bulletin of Environmental Contamination and Toxicology

Adsorption–Desorption, Persistence, and Leaching Behavior of Flufenacet in Alluvial Soil of India

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Received: 3 June 2000/Accepted: 15 October 2000

Flufenacet (N-(4-fluorophenyl)-N-(methylethyl)-2-[[5-(trifluoro methyl)-1,3,4-thiadiazole-2-yl]oxy]acetamide) with code name FOE 5043 is a new oxyacetamide herbicide introduced by M/s Bayer. It has been found effective for the control of a wide variety of economically relevant monocot weed species in maize, cereals, cotton, groundnut, potatoes, rice, soybeans, sunflower, tomatoes and other crops (Deege et al. 1995; Forster et al. 1997; Michel 1998). Flufenacet also exhibits excellent properties as a mix partner for herbicides controlling dicotyledonous weeds. It has been used in combination with metosulam, diflufenican and metribuzin (Brinkmann and Dahmen 1997; Diehl and Benz 1998; Kremer 1997). Adsorption-desorption behavior of pesticide, especially herbicides, in soil influences its bioefficacy and persistence. It is also an important factor governing the migratory behavior of the pesticide in various compartment of environment particularly the ground water. Therefore, studies on the adsorption-desorption, persistence, leaching, etc. are necessary to determine the impact of pesticide on the environment. Review of literature has revealed that these types of studies have not yet been carried out for flufenacet. The present study was undertaken with the objectives to determine the adsorption-desorption characteristics, persistence and leaching of flufenacet in alluvial soil of Delhi, under laboratory conditions.

MATERIALS AND METHODS

Fresh surface soil (0-15 cm depth) was collected from the fields of Indian Agricultural Research Institute, New Delhi, India, air-dried and sieved through 2 mm mesh screen. This soil (type inceptisol) was later used in various studies. The physico-chemical properties of the soil were: pH 7.1, organic carbon 0.34%, clay 19.7%, sand 64.7%, silt 15.6%, texture sandy loam, field capacity moisture content 20%. Analytical grade flufenacet (purity > 99.5%) was obtained from M/s Bayer India Ltd.

In all cases 0.01 N $CaCl_2$ aqueous solution was used as solvent for the herbicide solution. Stock solution of flufenacet (500 μg/mL) was prepared in acetone. An aliquot of stock solution containing required amount of flufenacet was transferred into the ground glass joint tube and left at room temperature (25±2°C) for the

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evaporation of acetone. The residues were dissolved in 0.01 N $CaCl_2$ solution and used for adsorption studies.

Preliminary kinetic studies were carried out to determine equilibrium adsorption time. Ground glass joint tubes containing 10 g of soil suspended in 20 mL of solvent matrix containing 500 µg flufenacet were shaken on a horizontal shaker. Sample were drawn after 1, 2, 4, 6 and 24 hr of shaking, centrifuged and the supernatant was analysed. Analysis showed that maximum adsorption took place within the first 3 hr. Therefore, 4 hr equilibration time was used in adsorption-desorption studies. Adsorption studies were carried out using batch equilibration technique. Soil samples (10 g), in duplicate, were equilibrated with 20 mL of flufenacet solution prepared in 0.01 N $CaCl_2$ matrix. The concentrations of flufenacet used for adsorption studies were 0.1, 0.5, 1, 2, 5, 10, 20 and 30 µg/mL. All the concentrations were below its water solubility (56 mg/L at 20°C). The tubes were shaken for 4 hr at room temperature (25±2°C). After equilibration the suspension was centrifuged at 2000 rpm for 10 min. A 10 mL aliquot of the supernatant was pipetted out in a separatory funnel, diluted with aqueous saturated NaCl solution and extracted with dichloromethane (3 x 30 mL). Combined dichloromethane extract was dried by passing through anhydrous Na_2SO_4 and evaporated using Kuderna-Danish evaporator (KDE). In addition, blanks i.e. pesticide in $CaCl_2$ solution without soil, were simultaneously processed to determine the pesticide loss during equilibration and processing. No significant loss of flufenacet was observed during 4 hr equilibration period and processing.

For desorption studies, samples in duplicate containing 600 µg of flufenacet in 20 mL of solvent matrix were equilibrated with 10 g soil similar to the adsorption studies. Samples were centrifuged and 10 mL supernatant was taken out for analysis. Fresh 10 mL $CaCl_2$ solution was added to replenish the drawn amount. The samples were resuspended with the help of a vortex mixer and a glass rod to scrap any soil sticking to the walls and again equilibrated for 4 hr. The procedure of desorption was repeated five times. Each aliquot was analyzed separately.

Persistence of flufenacet in alluvial soil was studied at 1 and 10 µg/g level. Initially 200 g of soil was fortified at 100 µg/g level with standard solution of flufenacet. The fortified dry soil was then diluted with untreated soil to give two different levels of treatment, 1 and 10 µg/g. Treated soil samples (20 g) were transferred to beakers. Required amount of water was added to the beakers to bring the soil to field capacity moisture level. Beakers were weighed separately and the field capacity moisture regime was maintained throughout the experiment by replenishing the lost water daily. To study persistence under submerged condition, 20 g of treated soil samples (10 µg/g level) were transferred to beakers and submerged with water. About 3 cm water layer was maintained above the soil. Beakers were weighed and again constant weight of the beakers was maintained by adding lost water daily. In all the cases control without pesticide treatment was maintained simultaneously. All the samples were incubated in BOD at 25±1°C.

Samples in triplicate were drawn along with control after 0, 3, 7, 10, 14, 30, 45, 60 and 90 days of incubation.

Samples kept at field capacity were dried at room temperature and mixed with 0.2 mL of liquid NH_3. After about 3 hrs, 0.5 g each of activated florisil and charcoal were added to the soil and mixed well. The mixture was dry packed into the glass column (50 x 2.5 cm id) containing 2 cm layer of anhydrous Na_2SO_4 at the bottom. Column was eluted with about 125 mL mixture of acetone-hexane (1:9) and extract was concentrated in KDE. Submerged samples were extracted repeatedly by shaking with acetone. Acetone was evaporated off and the aqueous phase was extracted with dichloromethane (3 x 30 mL). Organic layer was dried by passing through anhydrous Na_2SO_4 and evaporated off completely using KDE.

Leaching studies were carried out using PVC columns (50 x 7 cm id). Experiment was replicated twice along with the control. The PVC tubes were first cut longitudinally into two halves and then rejoined using adhesive tape, to allow easy separation of the column after completion of the leaching cycle. Lower end of the column was capped with polyethylene sheet and small holes were made with the help of pin to collect the leachate. Columns were filled with soil up to a height of 35 cm. Lower end of the column was dipped into water and the water was allowed to rise by capillary action for overnight. Ten gram of fortified soil containing 500 µg of flufenacet was spread uniformly at the top and leaching was started. A constant head of 2 cm water above the top of the soil was maintained throughout the experiment. About 2800 mL water was allowed to leach down the column under natural flow condition. Observed flow rate was 0.5 mL/min. Leachate fractions (about 250 mL each) were collected at different time intervals. These were filtered, diluted with aqueous NaCl solution and extracted with dichloromethane (3 x 50 mL). Dichloromethane layer was dried and concentrated as earlier.

At the end of leaching experiment, column soil was cut horizontally into seven cores of 5 cm each. Soil from each core was mixed well. Representative soil sample (about 100 g dry weight) from each core was taken in duplicate and extracted with acetone. Acetone was evaporated off and the residual aqueous portion diluted with aqueous saturated NaCl solution and extracted with dichloromethane (3 x 50 mL). Organic phase was dried and concentrated as earlier.

Extracts obtained from adsorption-desorption, persistence and leaching experiments were concentrated to dryness, residues dissolved in *n*-hexane and analyzed by GLC-ECD. Flufenacet residues were estimated on Hewlett Packard 5890 Series II Gas Chromatograph equipped with ^{63}Ni electron capture detector, auto injector, megabore HP-1 column (10 m x 0.53 mm id, 2.65 µm film thickness). The operating temperatures were: detector 300°C, injector port 280°C, oven programmed as 160°C for 9 min, temperature increased @ 30°C/min to

260°C and maintained for 3 min. The carrier gas was nitrogen (IOLAR I) with flow rate of 15 mL/min. Under these conditions the retention time was 7.4 minutes. The minimum level of determination from the water and soil matrix was 0.005 μg/g.

RESULTS AND DISCUSSION

Adsorption-desorption data are presented in Table 1. The amount of chemical adsorbed on the soil after equilibration was calculated from the difference between initial and equilibrium concentration in solution. K_d values were calculated by taking the ratio of concentration of adsorbed pesticide in soil (C_s) to the equilibrium concentration in solution (C_e). The K_d values ranged from 1.57 to 4.43, showing high adsorption of flufenacet on alluvial soil. As the initial concentration of flufenacet in solution increased from 0.1 to 2 μg/mL, there was gradual increase in K_d values. But thereafter K_d values decreased even with increasing initial concentration of flufenacet. Initially adsorption increased as the concentration in solution increased up to 2 μg/mL level. Beyond this level, however, it seems that limited adsorption sites restrict the adsorption.

Table 1. Adsorption-desorption of flufenacet on soil.

Adsorption				Desorption	
Initial Conc. (μg/mL)	Equilibrium Conc. (C_e) (μg/mL)	Adsorbed Conc. (C_s) (μg/mL)	Distribution Coefficient (K_d)	Equilibrium Conc. (C_e) (μg/mL)	Adsorbed Conc. After desorption (C_s)(μg/mL)
0.1	0.06	0.09	1.57	8.89	25.56
0.5	0.24	0.51	2.11	4.59	25.27
1.0	0.42	1.15	2.72	2.40	22.77
2.0	0.88	3.91	4.43	1.56	20.86
5.0	2.29	5.43	2.38	1.26	19.12
10.0	4.86	10.29	2.12		
20.0	9.84	20.33	2.07		
30.0	16.66	26.69	1.60		

Conc. – Concentration

Adsorption and desorption data were also fitted into the linearized form of the Freundlich equation, $\log C_s = \log K + 1/n \log C_e$, where C_s is the amount of flufenacet adsorbed (μg/g of soil), C_e is the equilibrium concentration in solution (μg/mL) and K and 1/n are the constants expressing sorption capacity and affinity, respectively. Regression equations between $\log C_s$ and $\log C_e$ were calculated by the least square technique. The adsorption-desorption data fitted well into Freundlich equation with r = 0.99 for adsorption and r = 0.94 for desorption (Figure 1). The value of constant $K_{ads} = 2.26$ revealed that soil has high capacity

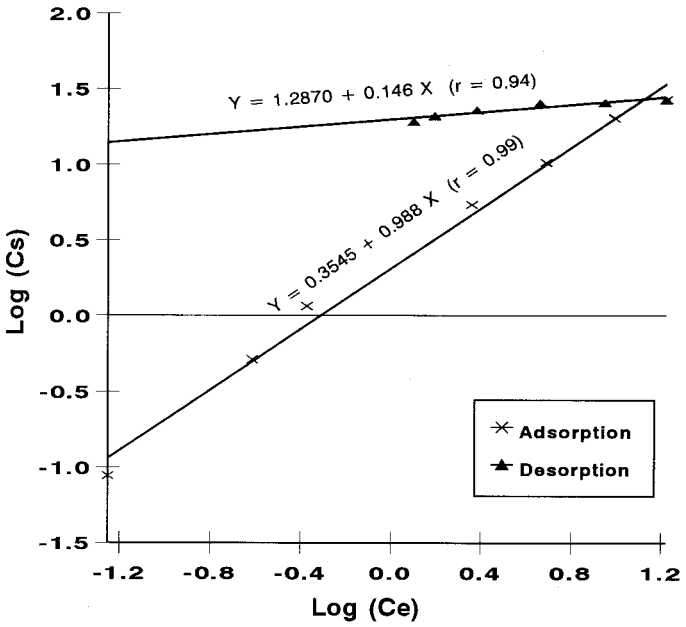

Figure 1. Adsorption - desorption of flufenacet on soil

for adsorption of flufenacet, whereas n_{ads} = 1.01 shows strong adsorption which is further confirmed by the hysteresis effect observed during desorption and free energy change (ΔG_{om}) during adsorption. The hysteresis coefficient (ratio of adsorption $1/n_{ads}$ and desorption $1/n_{des}$) was found to be 8.19, which is more than 1, showing that the adsorbed compound is difficult to desorb and desorption can not be predicted from the adsorption isotherm. Free energy change for adsorption as influenced by organic matter was calculated using the equation $\Delta G_{om} = -RT\ln K_{om}$, where ΔG_{om} = free energy change (Kcal/mol), R = gas constant (2.0 cal/Kmol), and K_{om} = K x 100/organic matter (%) and T = Kelvin temperature (298^{o}K). Calculated ΔG_{om} value was -3.317 Kcal/mol. The negative value of ΔG_{om} suggested that adsorption of flufenacet on soil was a spontaneous process. Further low value of ΔG_{om} revealed more or less physical nature of adsorption on the soil organic matter surface (Jana and Das 1997).

Persistence of flufenacet in soil was studied under two moisture regimes *viz.* field capacity and submerged condition. The initial deposits were 0.87 and 8.13 µg/g when fortified at the levels of 1 and 10 µg/g. Under both the conditions residues declined with time (Table 2). About 98.6% residues dissipated in 60 days at low level and 97.2% at higher level of fortification, at field capacity moisture. However, no residues were detected on 90th day at 1 µg/g level. At 10 µg/g level residues persisted beyond 90 days. Initially the dissipation of residues was faster

under submerged condition than field capacity. About 53.6% of the residues dissipated in 14 days as compared to 33.6% under field capacity. However, during later period, the dissipation under submerged condition became slower. This resulted in overall longer persistence. On 90th day, 95.5% residues dissipated under submerged condition as compared to 98.8% under field capacity.

Table 2. Persistence of flufenacet in soil under laboratory condition.

Days after application	Residues (µg/g) (Average of 3 replications)		
	Field capacity moisture level		Submerged condition
	1 µg/g level	10 µg/g level	10 µg/g level
0	0.87	8.13	8.13
3	0.67 (23.7)	7.67 (6.8)	6.49 (20.0)
6	0.58 (34.0)	6.49 (20.1)	4.79 (41.1)
10	0.50 (42.7)	5.80 (28.7)	4.03 (50.4)
14	0.46 (47.7)	5.40 (33.6)	3.77 (53.6)
29	0.16 (81.4)	2.76 (66.0)	3.09 (62.0)
45	0.05 (94.2)	0.99 (87.8)	1.88 (76.9)
60	0.01 (98.6)	0.23 (97.2)	1.20 (85.2)
90	BDL	0.09 (98.8)	0.37 (95.5)
Regression equation	Y = 0.019-0.0323 X	Y=0.979-0.0231X	Y = 0.626-0.134 X
Correlation Coeff..	0.99	0.99	0.99
Half-life (days)	9.3	13.0	22.5

Figures in parentheses denote per cent dissipation;
BDL – Below detection limit (< 0.005 µg/g); Coeff. - Coefficient

The dissipation of residues followed first order kinetics under both the conditions. The half life values calculated on the basis of first order kinetics were 9.3 days at 1 µg/g level and 13.0 days at 10 µg/g level, both under field capacity moisture and 22.5 days under submerged condition. The longer persistence of flufenacet (>90 days) could be attributed to its strong adsorption on alluvial soil.

Leaching experiment was carried out at room temperature. The collection of leachate (about 2800 mL) took around 3 days. The leaching data is presented in Figure 2 and 3. The analysis of leachate fractions (Figure 2) showed that no residues of flufenacet were present in leachate up to 1250 mL (5th fraction). The concentration of residues in leachate increased from 0.005 µg/mL in the 6th fraction to 0.049 µg/mL in the 12th fraction. Conversion of volume of leachate into equivalent rainfall revealed that continuous rainfall of about 32.5 cm (equivalent to ~1250 mL of leachate) will be required to leach flufenacet below 35 cm top layer of the soil.

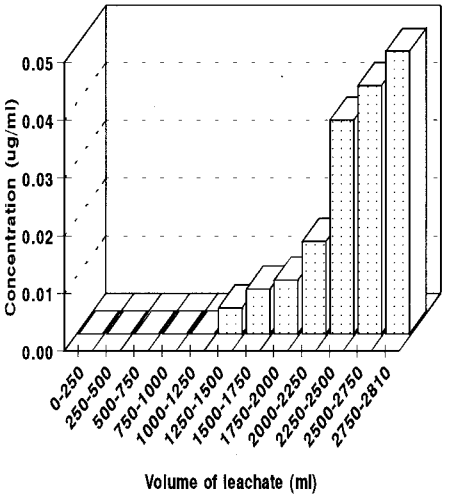

Figure 2. Flufenacet residues in column leachate

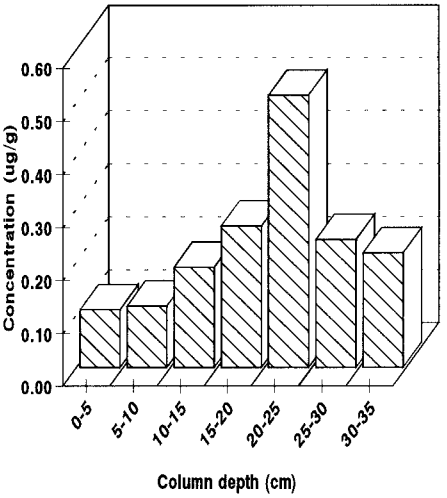

Figure 3. Mobility of flufenacet in soil column

The analysis of column soil (Figure 3) showed that after leaching of soil with ~2800 mL water, the flufenacet leached down along with water and got distributed throughout the column. The concentration of pesticide increased with depth up to 20-25 cm and then again decreased. The band of highest concentration of 0.336 μg/g was observed in the soil core at 20-25 cm depth. The data suggest that even after the continuous rainfall of 65 cm (equivalent to 2500 ml leachate), majority of the pesticide would still remain within 0-35 cm soil depth.

The studies reveal that flufenacet is strongly adsorbed on the alluvial soil. This strong adsorption may be responsible for its longer persistence in soil. It also affected the downward movement of flufenacet in soil. The leaching study showed that the possibility of leaching of flufenacet to ground water is extremely low under normal condition of average rainfall and compact nature of field soil.

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