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Degradation Dynamics of Flubendiamide in Different Types of Soils

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Abstract Residual dynamics of flubendiamide in three different types of soils were investigated under laboratory condition. Flubendiamide was applied at 5 and 10 μg g^{-1} for each soil and samples drawn periodically were analyzed on HPLC. The results showed that the degradation of flubendiamide in soils were followed first-order kinetics and its average half-lives in three kinds of soils were ranged from 37.62 to 60.21 days. The persistence of flubendiamide in soils significantly increased in the order of coastal soil > red and lateritic soil > new alluvial.

Keywords Flubendiamide · Desiodo flubendiamide · HPLC · Residues · Soil

Flubendiamide, N2-[1,1-dimethyl-2-(methylsulfonyl) ethyl]-3-iodo-N1-[2-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl) ethyl] phenyl]-1,2-benzenedicarboxamide), is a novel class of insecticide, having a unique chemical structure (Fig. 1) (Tohnishi et al. 2005). It provides superior plant protection against a broad range of economically important lepidopterous pest's species including diamondback moth, cabbage white butterfly, cluster caterpillar, *Helicoverpa* spp, *Heliothis* spp, *Spodoptera* spp, *Plutella* spp, *Trichoplusia* spp and *Hyrotis* spp (Tohnishi et al. 2005). Flubendiamide has a favourable ecological, ecotoxicological and environmental profile with low mammalian toxicity and no genotoxic, mutagenic or oncogenic properties (Shane 2006).

Recently, flubendiamide has been registered in India for rice and cotton cultivation. Being a new compound not much information is available on its method of analysis on flubendiamide and its metabolite desiodo flubendiamide soils in tropical Indian condition. There was no report of systematic investigation on the persistence of flubendiamide in soils from different agroclimatic zones of West Bengal, India. Therefore, the present investigation was designed to evaluate the persistence behavior of flubendiamide and its metabolite desiodo flubendiamide in three different types of soils under laboratory condition.

Materials and Methods

Analytical grade flubendiamide (98.5% purity) and desiodo flubendiamide (99.3% purity) obtained from M/s Rallis India Ltd, Bangalore, India. Organic solvents like acetonitrile, ethyl acetate, dichloromethane and hexane were glass distilled before use. Sodium sulfate was washed with acetone and then activated at 110°C for 4 h before use. HPLC grade solvents were procured from Merck India Ltd. These were filtered and de-gassed prior to use.

Individual stock solutions (1,000 μg mL^{-1}) of the analytical standard were prepared by dissolving 100 mg of each compound in 100 mL of acetonitrile and were stored at 4°C. Working standard solutions were prepared by appropriate serial dilutions in acetonitrile for the fortification of soil samples.

The soils of three different agro-climatic zones of West Bengal: New alluvial zone (Mondouri), Red and lateritic

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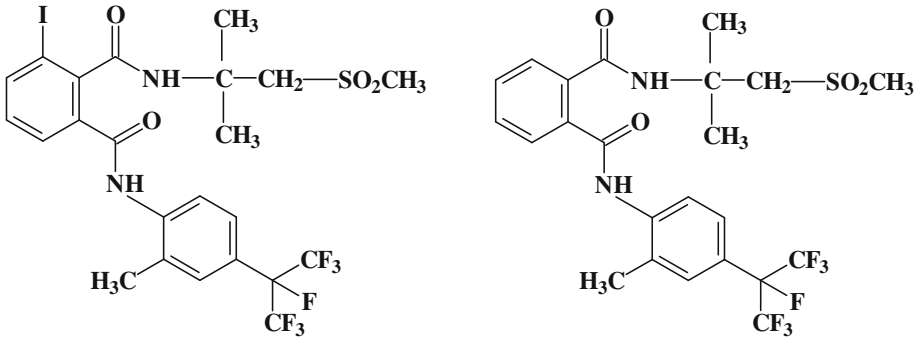

Fig. 1 The chemical structures of flubendiamide (**a**) and desiodo flubendiamide (**b**)

zone (Jhargram) and Coastal zone (Canning) were collected (1 kg) randomly from 6 to 8 places at a depth of 0–15 cm having no previous history of flubendiamide application. Soils were air dried, grounded and passed through a 2.0 mm sieve and sub-sampled by the usual methods of quartering. Soil texture, pH, organic carbon and CEC were determined (Table 1).

Degradation studies were carried out at under laboratory conditions (25 ± 1°C) and maintained at 90% relative humidity. The soil samples (20 g each) were placed in a conical flask, spiked with 5 and 10 μg g^{-1} of flubendiamide from standard stock solution (1,000 mg L^{-1}) of flubendiamide. Additional acetone was added to dip the soil, stirred with glass rod for uniform distribution of pesticide and then left undisturbed till complete evaporation of acetone. The dry soil was mixed thoroughly to obtain uniform fortification. The treated soil samples (20 g) were brought to the field capacity moisture level by adding water in each flask. Untreated control soil samples were also maintained simultaneously for each experiment. Three conical flask from each treatments were drawn along with the untreated control at different time intervals (upto 150 days) and analyzed for flubendiamide residues.

The fortified soil sample (20 g each) was taken in a conical flask (250 mL) and shaken for half an hour using a mechanical shaker with 100 mL acetonitrile and the extract was filtered through filter paper (Whatman No. 42.) mounted on a buchner funnel with 100 mL of acetonitrile. The pooled filtrate was transferred into a 500 mL round bottom flask and concentrated to about 50 mL using a rotary evaporator with a water bath at 40°C. The concentrated acetonitrile extracts was transferred quantitatively to a 500 mL separatory funnel. The sample was partitioned thrice with 100 mL hexane (saturated with acetonitrile) and the upper hexane layer was discarded each time. The lower acetonitrile layer was partitioned against dichloromethane (3 × 100 mL) by addition of 4% saturated NaCl solution. The combined organic layer was dried over anhydrous sodium sulphate and collected into a 500 mL pear shaped flask and concentrated to dryness on a rotary evaporator (40°C). The residues were reconstituted in mobile phase, filtered through 0.45 μm membrane filters and transferred to autosampler vials for the instrumental analysis in the HPLC–UV system.

Residues of flubendiamide and desiodo flubendiamide in soils were estimated by reverse phase HPLC system (Agilent 1200 series) with C-18 column, BDS Hypersil, 25 cm length × 4.6 mm i.d. and 0.5 mμ particle size was used for analysis. A mixture of acetonitrile:water (60:40, v/v) at 1 mL flow rate and detector set a 210 nm λmax was

Table 1 Physical properties of soils

Soil type	pH	CEC [C_{mol} (P^+) kg^{-1}]	EC (ds/m at 25°C)	OC (%)	Sand (%)	Silt (%)	Clay (%)
New alluvial	6.20	13.6	1.40	0.63	20.8	45.0	41.9
Red & lateritic	5.80	14.7	0.80	0.60	56.2	28.3	23.9
Coastal	7.80	14.8	4.60	0.93	23.0	26.7	35.2

Table 2 Recovery of flubendiamide and desiodo flubendiamide from soils

Soil type	Fortification Level (μg g^{-1})	Recovery percentage (Mean* ± SD)	
		Flubendiamide	Desiodo flubendiamide
New alluvial	0.01	87.47 ± 1.31	90.73 ± 1.57
	0.05	87.97 ± 1.26	87.51 ± 2.56
	0.10	88.58 ± 1.42	93.25 ± 1.18
Red & Lateritic	0.01	89.05 ± 1.56	91.37 ± 0.98
	0.05	86.77 ± 1.82	88.76 ± 1.21
	0.10	93.30 ± 1.08	96.60 ± 2.01
Coastal	0.01	89.62 ± 0.68	93.08 ± 0.78
	0.05	89.65 ± 1.59	89.45 ±1.23
	0.10	91.34 ± 1.23	94.34 ± 1.28

SD standard deviation

* Mean of three replicates

Table 3 Residues of flubendiamide and des-iodo in three different types of soil at 5 μg g^{-1}

Soil type	Pesticide	Average residues in μg g^{-1} ± SD at different days interval (% of dissipation)*								
		0	3	7	15	30	60	90	120	150
New alluvial	Flubendiamide	4.55	4.51	4.02	3.56	2.31	1.74	1.08	0.41	BDL
	Desiodo flubendiamide	0.17	0.21	0.28	0.20	0.13	0.10	0.05	BDL	BDL
	Total (Flu + Desiodo)	4.72 ± 0.06 (−)	4.72 ± 0.08 (0.0)	4.30 ± 0.0 (8.90)	3.76 ± 0.15 (20.34)	2.44 ± 0.08 (48.23)	1.84 ± 0.06 (61.02)	1.13 ± 0.12 (76.13)	0.41 ± 0.02 (91.31)	BDL (100)
Red and lateritic	Flubendiamide	4.38	4.28	3.99	3.55	2.48	1.42	1.21	0.54	BDL
	Desiodo flubendiamide	0.20	0.21	0.40	0.20	0.16	0.10	0.08	BDL	BDL
	Total (Flu + Desiodo)	4.58 ± 0.05 (−)	4.49 ± 0.01 (1.97)	4.38 ± 0.11 (4.29)	3.75 ± 0.10 (18.20)	2.64 ± 0.16 (42.36)	1.52 ± 0.08 (66.74)	1.28 ± 0.05 (71.98)	0.54 ± 0.02 (88.28)	BDL (100)
Coastal	Flubendiamide	4.51	4.41	4.35	3.94	2.71	1.94	1.28	0.65	BDL
	Desiodo flubendiamide	0.20	0.26	0.29	0.21	0.17	0.14	0.08	BDL	BDL
	Total (Flu + Desiodo)	4.71 ± 0.04 (−)	4.67 ± 0.03 (0.85)	4.64 ± 0.10 (1.49)	4.14 ± 0.12 (12.03)	2.88 ± 0.05 (38.78)	2.08 ± 0.09 (55.91)	1.36 ± 0.15 (71.05)	0.65 ± 0.04 (86.20)	BDL (100)

SD standard deviation, *BDL* below detection limit

* Mean of three replicates

Table 4 Residues of flubendiamide and des-iodo in three different types of soil at 10 μg g^{-1}

Soil type	Pesticide	Average residues in μg g^{-1} ± SD at different days interval (% of dissipation)*								
		0	3	7	15	30	60	90	120	150
New alluvial	Flubendiamide	9.05	8.97	8.00	7.08	5.61	4.35	3.19	1.56	0.74
	Desiodo flubendiamide	0.29	0.35	0.62	0.58	0.37	0.25	0.17	BDL	BDL
	Total (Flu + Desiodo)	9.34 ± 0.06 (−)	9.32 ± 0.11 (0.21)	8.62 ± 0.11 (7.71)	7.65 ± 0.17 (18.06)	5.98 ± 0.11 (35.94)	4.60 ± 0.12 (50.71)	3.36 ± 0.05 (63.99)	1.56 ± 0.05 (83.30)	0.74 ± 0.08 (92.08)
Red and lateritic	Flubendiamide	8.90	8.47	7.91	7.03	5.74	4.14	2.40	1.78	1.19
	Desiodo flubendiamide	0.34	0.39	0.84	0.44	0.29	0.24	0.15	BDL	BDL
	Total (Flu + Desiodo)	9.24 ± 0.02 (−)	8.86 ± 0.09 (4.08)	8.75 ± 0.05 (5.30)	7.47 ± 0.07 (19.19)	6.03 ± 0.09 (34.74)	4.38 ± 0.08 (52.56)	2.55 ± 0.03 (72.40)	1.78 ± 0.06 (80.74)	1.19 ± 0.04 (87.12)
Coastal	Flubendiamide	8.97	8.53	8.11	6.76	5.48	4.62	3.32	2.32	1.34
	Desiodo flubendiamide	0.39	0.53	0.56	0.41	0.36	0.25	0.12	BDL	BDL
	Total (Flu + Desiodo)	9.36 ± 0.15 (−)	9.06 ± 0.14 (3.21)	8.66 ± 0.15 (7.44)	7.17 ± 0.09 (23.43)	5.84 ± 0.22 (35.57)	4.87 ± 0.15 (47.93)	3.44 ± 0.11 (63.25)	2.32 ± 0.08 (75.18)	1.34 ± 0.05 (85.68)

SD standard deviation, *BDL* below detection limit

* Mean of three replicates

used for analysis of flubendiamide and desiodo flubendiamide showed sharp peak at 9.77 and 7.66 min respectively under the described HPLC conditions. The quantification was done using external working standard calibration curves. The limit of detection (LOD) was 0.003 μg g^{-1}, limit of quantification (LOQ) was 0.01 μg g^{-1} for the analysis of these samples.

The efficiency of the method was evaluated by carrying out a recovery experiment. The untreated soil samples (20 g air dry), in triplicate, were fortified with working standard solution to furnish concentrations of 0.01, 0.05, and 0.1 μg g^{-1}. After spiking, samples were allowed for 30 min at ambient temperature to evaporate the acetonitrile, and then processed. The control samples were processed by a similar stepwise procedure to check for interference from the matrix. They were processed and analyzed by HPLC as described above.

The residue data were subjected to regression analysis and the fit of the data to first order kinetics ($Ct = C_o e^{-Kt}$) was confirmed by testing the statistical significance of correlation coefficient. The half-life values were calculated from regression analysis.

Results and Discussion

The recoveries of flubendiamide and desiodo flubendiamide from soil samples fortified at 0.01, 0.05 and 0.1 μg g^{-1} level varied from 86%–93% to 87%–96% respectively (Table 2). Since recoveries were more than 80%, the residue data has not been corrected for the recoveries.

Persistence of flubendiamide in three different types of soils under laboratory condition was studied at two levels of application 5.0 and 10.0 μg g^{-1}. The residue data for different soils were presented in Table 3 and 4. The initial concentrations of flubendiamide residues when applied at 5 and 10 μg g^{-1} in new alluvial soil, red and laterite soils, and coastal soil were 4.72, 4.58 and 4.71 μg g^{-1} and 9.34, 9.24, and 9.36 μg g^{-1} respectively. After 30 days of application, the residues remaining in different soils were in the range of 2.44, 2.64 and 2.88 μg g^{-1} and 5.98, 6.03 and 5.84 μg g^{-1} respectively, recording a loss of 38.78%–40.18%. The residues were further declined to 1.13, 1.28 and 1.36 μg g^{-1} and 3.36, 2.55 3.44 μg g^{-1} with 76.13%, 71.98% and 71.05%, and 63.99%, 72.40% and 63.25% dissipation respectively after 90 days application. The dissipation pattern of flubendiamide in three different soils under laboratory condition also indicated a rapid and strong adsorption of flubendiamide by these soils and little adsorbed material is released back into the aqueous phase, which seems to be correlated with clay and organic matter content of the soil.

The dissipation of flubendiamide in different soils followed first-order kinetics. The calculated half-life values ($T_{1/2}$) were ranged from 37.62–50.17, 43–50.17 to 50.17–60.21 days for new alluvial, red and laterite, and coastal soil, respectively. From the results, it was found that comparatively higher dissipation was observed in new alluvial soil than that exhibited in red and laterite and coastal soil in both the doses. The persistence of flubendiamide was in the order of coastal soil > red and lateritic soil > new alluvial soil. It appears that little differences in the dissipation kinetics of three soils were attributed to differences in soil pH, texture and the ability of indigenous microorganism to transform the insecticide.

The persistence data of all the three soils further revealed that flubendiamide dissipation rate was quite slow in coastal soil as compared to other two soils which might be due to high clay and higher organic matter content of the soil. Organic matter may bind flubendiamide or may form complex structure which prevents further microbial activity on the compound. Thus, the present study concludes that persistence of flubendiamide is more in coastal than neutral to acidic soil. Furthermore, low water solubility (Tsubata et al. 2007) of flubendiamide gives an indication of low potential for mobility in the soil (Shane 2006). Hence probability of contamination of ground water by flubendiamide is minimal.

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