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Effect of Light and pH on Persistence of Flubendiamide

Shaon Kumar Das · Irani Mukherjee

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Abstract Persistence of flubendiamide in soil as affected by UV and sunlight exposure and in water as affected by pH was studied. At field capacity moisture regime, soil was treated with flubendiamide and exposed to UV and sunlight. Dissipation for the pesticide followed mono-phasic first order kinetics. Residues of flubendiamide, as thin film on petri-plates and soil thin film, dissipated with half-lives of 7.0 and 9.1 days under UV light and 12.0 and 19.1 days under sunlight, respectively. Residues of flubendiamide dissipated faster under UV light as compared to sunlight. Persistence study in aqueous medium under different pH condition indicated that flubendiamide residues persisted in water beyond 250 days with half-lives ranging from 250.8 to 301.0 days. Dissipation in water was faster at pH 4.0 ($T_{1/2}$ 250.8 days), followed by pH 9.2 ($T_{1/2}$ 273.6 days) and 7.0 ($T_{1/2}$ 301.0 days).

Keywords Flubendiamide · Dissipation · Soil · Ultra violet light · Sunlight · pH

It has been reported in literature that among various biotic and abiotic transformation processes, photodegradation is an important factor influencing the fate of pesticides in the field (Konstantinou et al. 2001). In practice it has been observed that pesticides persist longer under laboratory condition as compared to field condition (Sanyal et al. 2000; Ganier et al. 1996; Fernandez et al. 2001). Surface residues, following foliar spray degrade faster than the translocated residues inside plant matrix even though physiological activity is more inside the plant matrix (Scheunert 1992). Faster degradation of highly persistent DDT under sunlight as compared to samples kept under dark condition has already been reported (Miller and Zepp 1983). All these observations emphasized on the important role played by light in pesticide degradation. On the other hand, persistent pesticides have the potential of affecting the health of soil and aquatic bodies due to their toxic nature. In aquatic bodies, pH of the medium plays a great role for degradation of pesticide due to hydrolysis reaction. It has been suggested that beside photodegradation, investigation of their hydrolytic fate in aqueous medium might contribute towards a better understanding of pesticide behavior in the environment (Klopffer 1992). So, more information on the degradation time of a pesticide, and consequently, on its activity and environmental fate, can be obtained by studying the kinetics of both photolysis and hydrolysis reaction (Scheunert 1992).

Flubendiamide, N′-[1,1-dimethyl-2-(methylsulphonyl) ethyl]-3-iodo-N-{4-[2,2,2tetrafluoro- 1-(trifluoromethyl) ethyl]-0-tolyl} phthalimide belongs to a new chemical class, the phthalic acid diamide, and is widely used against lepidopteran pests on a variety of annual and perennial crops. It provides superior plant protection against a broad range of economically important lepidopterous pests including *Helicoverpa spp*, *Heliothis spp*, *Spodoptera spp*, *Plutella spp*, *Trichoplusia spp* and *Hyrotis spp*. Flubendiamide has a favourable ecological, ecotoxicological and environmental profile with low mammalian toxicity and no genotoxic, mutagenic or oncogenic properties (Shane 2006). The log P and vapour pressure are approximately 4.2 and $<1 \times 10^{-1}$ mPa (25°C), respectively. Flubendiamide is only slightly soluble in water (29.9×10^{-6} g L^{-1} at 20°C). Flubendiamide has been recently introduced in India by Bayer Crop Science for use on major vegetable crops.

S. K. Das · I. Mukherjee (✉)
Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India
e-mail: mukrj_irani@yahoo.com

The effect of light and pH on persistence of flubendiamide under subtropical conditions has not been reported in literature till date. Therefore, the present experiments were conducted to study the effect of light (sunlight and UV light) and pH on persistence of flubendiamide.

Materials and Methods

Soil required for the study was collected from the plough layer (0–15 cm depth) of the research farm of Indian Agricultural Research Institute, New Delhi, India, with no history of pesticide application. It was air-dried in the shade, ground, sieved through a 2-mm mesh screen. The physico-chemical properties of the soil (type inceptisol) were: pH 8.18, organic carbon 0.16% measured by using the Walkley and Black method (1965), clay 8.33%, sand 72.12%, silt 19.55% measured by employing the Bouyoucos hygrometer (1967), texture sandy loam and field capacity moisture content 20%. Analytical grade flubendiamide was obtained by extraction from the formulation (Fame 480 SC) provided by Bayer India Ltd (New Delhi, India). It was re-crystallized from methanol to obtain the analytical standard. The purity of the compound was checked by its melting point (220°C) and confirmed by TLC. The structure was characterized by NMR and confirmed by LC–MS fragmentation pattern with literature values (Fig. 1). The stock solution of flubendiamide of 1000 mg L^{-1} was prepared in acetonitrile and stored at 4°C. Working standards were prepared by appropriate dilutions. Organic solvents like acetone, dichloromethane and methanol were glass distilled before use. Buffer tablets were procured from M/s Qualigen India. 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.

Soil (100 g) was taken in a beaker and required quantity of standard stock solution (1,000 mg L^{-1}) of flubendiamide was added to get 100 mg kg^{-1} concentration. 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. This fortified soil was diluted with untreated soil in the ratio 1:9 to get 10 mg kg^{-1} fortification level and the soil was mixed thoroughly. The homogeneity of treated soil was tested by randomly drawing three samples from the treated soil and analyzing them. Since there was not much variation among replicates, the treated soil was considered homogeneous. The treated soil samples (2 g) were transferred and spread uniformly in petri-plates (5 cm i.d.) and soil was brought to the field capacity moisture level by adding 0.4 mL water in each plate. All the petri-plates were weighed and divided into two sets. One set of petri-plates was exposed to UV light (18″ tube, 15 W, 254 nm) for 6 h in a closed chamber and the second set was kept in open under sunlight. The water lost was replenished daily by weighing the petri-plates. Samples kept under sunlight and UV light was exposed for 6 h daily.

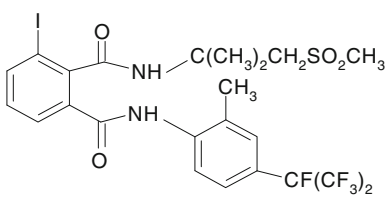

Fig. 1 Flubendiamide

To study the dissipation of flubendiamide in UV and sunlight, experiment was conducted with thin film of pure compounds on glass surface. Standard solution of flubendiamide (2 mL, 10 mL L^{-1}) was spread on petri-plates (5 cm i.d.). Petri-plates were kept on flat surface and left undisturbed for evaporation of solvent. The plates were divided into two sets. One set of petri-plates was exposed to UV light (18″ tube, 15 W, 254 nm) for 6 h in a closed chamber and the other was kept in open under sunlight. Samples were exposed to sunlight/UV light for 6 h daily. Samples in duplicate from each treatment were drawn at different time intervals and processed. Soil samples collected from different experiments were taken in beaker and enough acetone was added to dip the soil. The samples were stirred with glass rod and kept for 30 min with intermittent shaking. The contents were filtered using Whatman filter paper No. 1, soil was transferred back to beaker and re-extracted two more times using fresh 50 mL acetone each time. Acetone extracts were pooled and concentrated using rotary evaporator. The concentrated extract was transferred to separatory funnel, diluted with saline solution (10%, 100 mL) and exchanged into dichloromethane (3 × 30 mL). The combined dichloromethane extract was passed through anhydrous sodium sulfate. The extract was evaporated to dryness using rotary evaporator and the residues dissolved in HPLC grade acetonitrile. Samples of thin film were directly dissolved in acetonitrile, filtered and analysed by HPLC. Persistence of flubendiamide in water was studied at three different pHs, 4, 7 and 9.2. Buffer solutions of pH 4.0, 7.0 and 9.2 (~800 mL each) were prepared by dissolving corresponding buffer tablets (Qualigen make) in distilled water (one buffer tablets/100 mL water). Buffer solutions were fortified at 1 μg mL^{-1} level using stock solution of analytical grade flubendiamide at 1 μg mL^{-1} level concentration. Samples were drawn on 0, 3, 5, 7, 10, 15, 30, 45,

60, 90 and 120 day intervals. Treated solutions were transferred into 50 mL capacity ground glass joint tubes (20 mL/tube) and kept in BOD incubator at 25± 1°C and maintained at 90% relative humidity. On each sampling day, samples in triplicate were drawn from each treatment. Samples of water were transferred in a separatory funnel, diluted with saline solution (10%, 100 mL) and partitioned thrice with dichloromethane (3 × 30 mL). The dichloromethane extract was passed through anhydrous sodium sulfate. The extract was evaporated to dryness using rotary evaporator and the residues dissolved in HPLC grade acetonitrile.

Residues of flubendiamide were estimated by HPLC system (Merck-Hitachi)—Consisting of a L-7100 (computer operated dual pump), a L-7400 (UV detector) and a L-7200 (Auto sampler), HPLC column (30 cm)—Lichrospher, RP-18 (5 µm) was used for analysis. A mixture of acetonitrile -water (70: 30, v/v) was used as the mobile phase, with a flow rate of 0.5 mL min^{-1}. The injection volume was 10 µL and the wavelength was set at 210 nm (λ_{max}, determined by using spectrophotometer. Flubendiamide eluted at 10.53 min under these conditions. The limit of detection (LOD) was 0.01 mg kg^{-1}, limit of quantification (LOQ) was 0.025 mg kg^{-1} for the analysis of these samples. A representative HPLC chromatogram showing well resolved peak of the flubendiamide is presented in Fig. 2.

The residue data were subjected to regression analysis and the fit of the data to first order kinetics ($Ct = Coe^{-Kt}$) was confirmed by testing the statistical significance of correlation coefficient. The half-life values were calculated from dissipation constant calculated from regression analysis. The efficiency for analysis in light was evaluated by carrying out recovery experiment. The untreated soil samples (2 g air dry), in triplicate, were fortified, processed and analyzed by HPLC as described above. The recoveries of flubendiamide from soil samples fortified at 0.05, 0.5, 1.00 µg g^{-1} level were found to be 88 ± 2.67, 93.7 ± 1.52 and 94.06 ± 1.78. Since recoveries were more than 90%, the residue data has not been corrected for the recoveries.

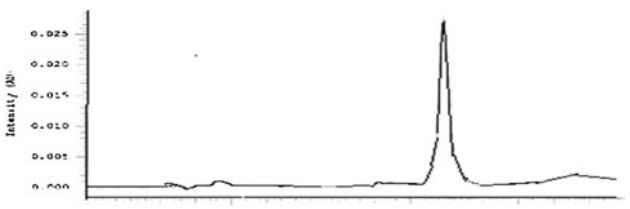

Fig. 2 HPLC chromatogram of flubendiamide

Results and Discussion

Persistence of flubendiamide under sunlight as soil thin film and thin film is presented in Table 1. The data shows that the average residues after 0, 5, 10 and 15 days were 9.95, 8.55, 7.15, 5.8 mg/kg in soil thin film and 9.96, 8.2, 6.8, 4.5 µg mL^{-1} in thin film on petri-plates (Table 1). Within 15 days, 41.7 and 58.8% of flubendiamide disappeared from soil thin film and thin film on petri-plates, respectively. Dissipation was faster in thin film on petri-plates than in soil thin film (Table 1). The residue data was subjected to first order kinetics using regression analysis. The half-life of flubendiamide under sunlight is found to be 19.1 days in soil thin film and 12.0 days in thin film on petri-plates (Table 2). The regression equation for first order dissipation is shown in Table 2. Dissipation kinetics of flubendiamide under UV light and Sunlight has been shown in Fig. 3.

Persistence study of flubendiamide was also studied under UV light as soil thin film and thin film on petri plates. The residue and the dissipation data obtained at different time intervals are presented in Table 1. The dissipation was fast under UV-light conditions as thin film on petri-plates as compared to soil thin film. Persistence data shows that within 15 days 75.5 and 84.9% dissipated from soil thin film and from thin film on petri plates, respectively. The average residues recovered after 0, 5, 10 and 15 days were 9.94, 7.59, 4.77, 2.43 mg kg^{-1} in soil thin film (Table 1) and 9.96, 6.53, 3.1, 1.5 µg mL^{-1} in thin film on petri-plates (Table 1) respectively. The residue data was subjected to first order kinetics using regression analysis. The half-life under UV light was found to be 9.1 days in soil thin film and 7.0 days in thin film on petri-plates (Table 2). The regression equation for first order dissipation is shown in Table 2. Longer persistence in soil thin film could be due to the adsorption of pesticides on soil surface. Katagi (2004) has also reported that photodegradation of pesticides on soil surface is influenced by adsorption to clay minerals or solubilization to humic substances.

Dissipation studies on flubendiamide under sunlight and UV light revealed that the compound dissipates faster in UV light as compared to sunlight, however dissipation slows down in the presence of soil matrix.

The persistence of flubendiamide in water was studied under laboratory conditions at three different pH, 4.0, 7.0 and 9.2 at 1.0 µg mL^{-1} fortification level. The residue data along with the percentage of dissipation at different time intervals are presented in Table 3. The initial deposits at pH 4.0, 7.0 and 9.2 were found to be 0.971, 0.965 and 0.964 µg mL^{-1}, respectively. The percent dissipation recorded by 15 day was 4.0–5.4, while by 60 day, 10.3–13.0% was observed and 18.5–22.3% by 120 day. The overall rate

Table 1 Persistence of flubendiamide as soil thin film and thin film under UV light and sunlight

Days	*Average residues ± SD			
	Sunlight		UV light	
	Soil thin film (mg kg^{-1})	Thin film on petri-plate (mg kg^{-1})	Soil thin film (mg kg^{-1})	Thin film on petri-plate (mg kg^{-1})
0	9.95 ± 0.03	9.96 ± 0.01	9.94 ± 0.14	9.96 ± 0.02
1	9.67 ± 0.04 (2.8)	9.40 ± 0.06 (5.6)	9.47 ± 0.15 (4.7)	9.25 ± 0.07 (7.1)
3	9.11 ± 0.06 (8.4)	8.91 ± 0.04 (10.6)	8.53 ± 0.18 (14.1)	7.89 ± 0.2 (20.7)
5	8.55 ± 0.12 (16.3)	8.20 ± 0.03 (17.6)	7.59 ± 0.13 (23.6)	6.53 ± 0.08 (34.4)
7	7.99 ± 0.11 (19.7)	7.51 ± 0.03 (24.7)	6.18 ± 0.20 (37.8)	5.13 ± 0.10 (48.5)
10	7.15 ± 0.12 (28.1)	6.82 ± 0.11 (31.7)	4.77 ± 0.04 (52.0)	3.10 ± 0.14 (68.8)
15	5.80 ± 0.13 (41.7)	4.50 ± 0.08 (58.8)	2.43 ± 0.09 (75.5)	1.50 ± 0.11 (84.9)

* Average of three replicates; Figures in parenthesis shows % dissipation

Table 2 Regression equation and half-life for first order dissipation of flubendiamide

Treatment	Dissipation type	Regression equation Y=	K values	R^2	$T_{1/2}$ (days)
Sunlight					
Thin film	Single phase	−0.025x + 0.995	0.058	0.997	12.0
Soil thin film	Single phase	−0.0157x + 1.004	0.036	0.994	19.1
UV light					
Thin film	Single phase	−0.043 + 1.046	0.099	0.982	7.0
Soil thin film	Single phase	−0.033x + 1.04	0.076	0.996	9.1

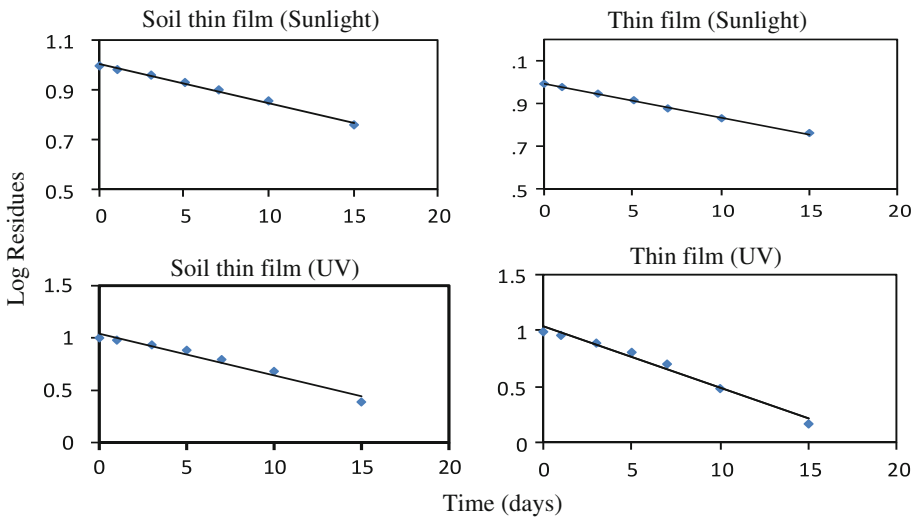

Fig. 3 Dissipation kinetics of flubendiamide under sunlight and UV light

of dissipation was found to be faster in case of pH 4. (22.3%) followed by pH 9.2 (21.0%) and pH 7 (18.5%).

The data was subjected to first order kinetics using regression analysis. The calculated regression equations and half life values along with correlation coefficient and K values are presented in Table 4. In all the cases the correlation coefficients were found to be >0.90.

The half life values calculated from the forced single phase first order rate dissipation kinetics varied from 250.8 to 301 days (Table 4). Results revealed that flubendiamide dissipated faster under acidic pH ($T_{½}$, 250.8 days) than under basic pH ($T_{1/2}$, 273.6 days). Slowest dissipation was recorded at neutral pH ($T_{1/2}$, 301 days).

Results revealed that flubendiamide dissipated faster under acidic pH than under basic pH. Slowest dissipation was recorded at neutral pH. The faster dissipation of flubendiamide in water under acidic and basic pH conditions could be due to the hydrolysis of the two amide linkage in the molecule.

Table 3 Persistence of flubendiamide in water under different pH conditions

Days	*Average residues (μg mL^{-1}) ± SD		
	pH 4	pH 7	pH 9.2
0	0.971 ± 0.01	0.965 ± 0.06	0.964 ± 0.05
3	0.969 ± 0.07 (0.2)	0.963 ± 0.03 (80.1)	0.961 ± 0.06 (0.3)
5	0.957 ± 0.04 (1.4)	0.958 ± 0.06 (0.7)	0.952 ± 0.01 (1.2)
7	0.952 ± 0.02 (1.9)	0.952 ± 0.08 (1.3)	0.950 ± 0.03 (1.4)
10	0.942 ± 0.03 (3.0)	0.933 ± 0.01 (3.3)	0.921 ± 0.05 (4.4)
15	0.921 ± 0.06 (5.1)	0.926 ± 0.02 (4.0)	0.912 ± 0.08 (5.4)
30	0.85 ± 0.07 (7.0)	0.905 ± 0.06 (6.2)	0.881 ± 0.09 (8.6)
45	0.817 ± 0.01 (9.7)	0.876 ± 0.09 (9.2)	0.858 ± 0.01(10.9)
60	0.760 ± 0.09 (11.8)	0.846 ± 0.07 (10.3)	0.818 ± 0.06 (13.0)
90	0.721 ± 0.05 (16.3)	0.833 ± 0.01(13.7)	0.771 ± 0.02 (15.7)
120	0.654 ± 0.03 (22.3)	0.777 ± 0.03 (18.5)	0.721 ± 0.07 (21.0)

* Average of three replicates; Figures in parenthesis shows % dissipation

Table 4 Regression equation and half-life for first order dissipation of flubendiamide

pH	Regression equation Y=	K value	R^2	$T_{1/2}$ (days)
4.0	−0.0012 × –0.014	0.0028	0.984	250.8
9.2	−0.0011 × –0.018	0.0025	0.988	273.6
7.0	−0.001 × –0.018	0.0023	0.974	301.0

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