

Persistence of chlorfluazuron in water at different pH levels

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ABSTRACT

Dissipation kinetics of chlorfluazuron was studied in water maintained at different pH. Chlorfluazuron was spiked in water at the rates of 1.0 and 2.0 $\mu\text{g ml}^{-1}$. Water samples collected on 0 (2h after application), 3, 7, 15, 30, 60 and 90 days after application and partitioned with ethyl acetate in the respective sampling date. Samples were processed and analyzed using HPLC equipped with Photo Diode Array detector. It was found that chlorfluazuron residue degraded with increment of time and followed first order kinetics in the entire study. The calculated half-life values of chlorfluazuron in water samples were in the range between 19.55-22.81 days at acidic pH, 16.10-18.47 days at neutral pH and 10.31-13.26 days at alkaline pH irrespective of doses. The stability of this particular molecule was decreased with the increase in pH of water.

Keywords: Chlorfluazuron, dissipation, half-life, pH, water

Chlorfluazuron insecticide, belongs to benzophenyl urea group (figure 1), can work as potent chitin synthesis inhibitor and controls various lepidopteran larvae including diamond back moth (DBM). It has very little or no negative impact on natural enemies and pollinators insects and can be used in integrated pest management programmes. Chlorfluazuron possesses ovicidal activity against adult german cockroach (*Blattella germanica*), and the common cutworm (*Spodoptera litura*)^{1,2} and has also been evaluated for uses in non-crop applications such as fly control³ and for use as part of a termite bait matrix^{4,5} which may extend the use of this mature compound. In India, it is registered against diamond back moth and tobacco leaf eating caterpillar in cabbage @ 75 g a.i. ha⁻¹ and american bollworm and tobacco leaf eating caterpillar in cotton @ 75 g a.i. ha⁻¹. Besides its potent insecticidal property, chlorfluazuron may possess toxicity risk to the non-target organism especially human being. It is very essential to estimate the extent of chlorfluazuron residues that can be found in various substrates like soil, water etc. Thus, the present experiment has been designed to find out the persistence of chlorfluazuron in water maintained at different pH under laboratory simulated condition. The results could be utilized for further research in determining the fate of this herbicide in water system in field conditions.

MATERIALS & METHOD

The present investigation has been designed to find out the persistence of chlorfluazuron in water maintained at three different pH viz. 4.0 (acidic), 7.0 (neutral) and

9.2 (alkaline) under laboratory simulated condition. Chlorfluazuron analytical standard (10 mg) as well as chlorfluazuron 5.4 per cent EC formulation (~185.19 mg), supplied by M/S United Phosphorus Ltd., were separately taken in two 100 ml volumetric flasks. The volumes were made up to the mark with HPLC grade methanol to prepare stock standard of 100 $\mu\text{g ml}^{-1}$ of each formulation & technical grade. Necessary dilutions were made from these standards as and when required. The pH of water was adjusted using buffer capsules of pH 4.0, 7.0 and 9.2. One capsule is required for 100 ml of distilled water to maintain the above mentioned pH. Distilled water (200 ml) was added in a series of 250 ml conical flask and two capsules were added to each of the conical flask. The conical flasks were then left at room temperature (21-41.5°C) for overnight for homogeneous mixing. Water samples of different pH (200 ml) were taken in 250 ml conical flasks. Then 2 ml and 4 ml of the 100 $\mu\text{g ml}^{-1}$ stock solution of chlorfluazuron 5.4 per cent EC were added to conical flasks separately. The initial concentrations of chlorfluazuron in water became 1 $\mu\text{g ml}^{-1}$ (T₁) and 2 $\mu\text{g ml}^{-1}$ (T₂) respectively. For each treatment three replicates were taken along with untreated control containing buffer solution. Samples (three replicates) were processed for analysis of chlorfluazuron residues at intervals of 0 (2h after application), 3, 7, 15, 30, 60 and 90 days after application.

Water sample (200 ml) in the respective sampling date was taken in a 500 ml separatory funnel. This was partitioned thrice with 200 (100+50+50) ml of ethyl acetate. Then, ethyl acetate fraction was collected

through anhydrous Na_2SO_4 . After that, this combined fraction was evaporated to dryness in rotary vacuum evaporator at 40°C and the final volume was reconstituted with HPLC grade methanol. Finally, it was analyzed in HPLC equipped with Photo Diode Array (PDA) detector.

Peerless Basic C18 (250 mm X 4.6 mm) column was used for chromatographic separation of chlorfluazuron in HPLC. Methanol is selected as mobile phase in the system at a flow rate of 1.0 ml min^{-1} . Under these working conditions, chlorfluazuron was detected (at $\lambda_{\text{max}} = 255 \text{ nm}$) at the retention time of $3.9 \pm 0.20 \text{ min}$ (figure 2). The LOD and LOQ of the method were determined as 0.05 and $0.10 \mu\text{g g}^{-1}$ respectively (Fig. 3).

Recovery studies were carried out in order to establish the reliability of the analytical methods and to judge the efficiency of extraction and clean up step of the present study. Water samples, maintained at different pH, were fortified separately with chlorfluazuron 5.4 per cent EC at 0.10 , 0.50 and $1.00 \mu\text{g ml}^{-1}$ level.

RESULTS AND DISCUSSION

Average recoveries of chlorfluazuron from water fortified at 0.10 , 0.50 and $1.00 \mu\text{g ml}^{-1}$ were 92.67 per cent at pH 4.0 , 91.33 per cent at pH 7.0 and 92.00 per cent at pH 9.2 as shown in table 1. Hence the analytical method was quite satisfactory and adopted for the present study.

The mean residue, percent dissipation, regression equation and half-life values of chlorfluazuron in water samples maintained at different pH at different day's interval are presented in table 2. It was observed that the initial concentrations of chlorfluazuron degraded with increment of time and followed first order kinetics in the entire study. Residues were below detectable limit

(BDL) of $0.10 \mu\text{g ml}^{-1}$ in all untreated control samples (T_3) throughout the study.

Chlorfluazuron were found in the range between 0.99 - $1.96 \mu\text{g ml}^{-1}$ as initial residue and half-life values were between 19.55 - 22.81 days irrespective of T_1 ($1 \mu\text{g ml}^{-1}$ of water) and T_2 ($2 \mu\text{g ml}^{-1}$ of water) in water samples maintained at pH 4.0 . The initial residues dissipated more than 60 per cent within 30 days and the residues were below detectable limit (BDL) on 90^{th} day after application irrespective of the treatment.

At pH 7.0 , initial residue and half-life value of chlorfluazuron were ranged from 0.97 - $1.96 \mu\text{g ml}^{-1}$ and 16.10 - 18.47 days irrespective of T_1 ($1 \mu\text{g ml}^{-1}$ of water) and T_2 ($2 \mu\text{g ml}^{-1}$ of water). The initial residues dissipated to around 70 per cent in case of T_1 and 60 per cent in case of T_2 within 30 days after application. The residues were below detectable limit (BDL) on 60^{th} day and 90^{th} day after application for T_1 and T_2 respectively.

At pH 9.2 , initial residue and half-life value of chlorfluazuron were ranged from 0.94 - $1.92 \mu\text{g ml}^{-1}$ and 10.31 - 13.26 days irrespective of T_1 ($1 \mu\text{g ml}^{-1}$ of water) and T_2 ($2 \mu\text{g ml}^{-1}$ of water). The initial residues dissipated more than 55 per cent within 15 days and the residues were below detectable limit (BDL) on 60^{th} day after application irrespective of the treatment.

The results of this particular experiment showed that the initial concentration of chlorfluazuron was found to be in the range between 0.94 - $0.99 \mu\text{g ml}^{-1}$ and 1.92 - $1.96 \mu\text{g ml}^{-1}$ irrespective of T_1 ($1 \mu\text{g ml}^{-1}$ of water) and T_2 ($2 \mu\text{g ml}^{-1}$ of water) and pH. The calculated half-life values of chlorfluazuron in different water samples were in the range between 19.55 - 22.81 days at acidic pH, 16.10 - 18.47 days at neutral pH and 10.31 - 13.26 days at alkaline pH irrespective of doses. Results of chlorfluazuron persistence in water maintained at

Table 1: Recovery study of chlorfluazuron in water samples of pH 4.0, pH 7.0 and pH 9.2

Fortification level ($\mu\text{g ml}^{-1}$)	Recovery (%)*		
	pH 4.0	pH 7.0	pH 9.2
0.05	93.00	89.00	87.00
0.10	94.00	92.00	94.00
1.00	91.00	93.00	95.00
Average recovery (%)	92.67	91.33	92.00
Recovery factor	1.08	1.10	1.09

*Mean of three replications

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different pH showed that the compound dissipates slight quicker in alkaline pH than in neutral and acidic pH. The stability of this particular formulation was decreased with the increase in pH of water though the decrement was not so higher. At the end of incubation (90 days), the residue remaining in water was found below detectable limit irrespective of doses and pH.

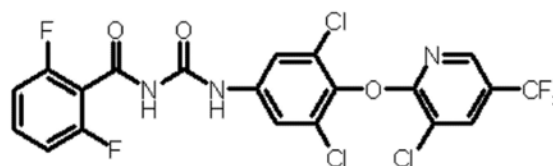


Fig. 1: Structure of chlorfluazuron

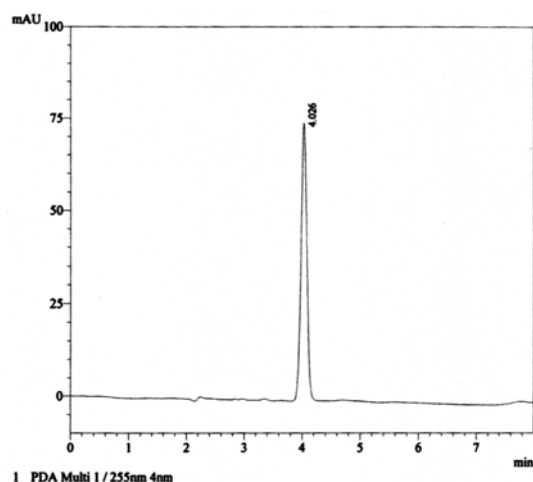


Fig. 2: Chromatogram of chlorfluazuron standards under HPLC operating conditions

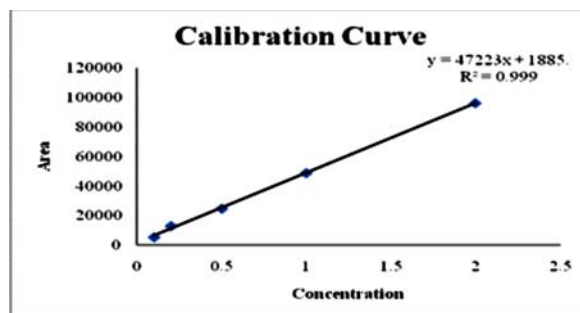


Fig. 3: Calibration curve of area corresponding to different concentrations of analytical standard of chlorfluazuron

Table 2: Dissipation of chlorfluazuron in water samples of different pH at different day's interval

Days	Residues ($\mu\text{g ml}^{-1}$)					
	Acidic water (pH 4.0)		Neutral water (pH 7.0)		Alkaline water (pH 9.2)	
	$1 \mu\text{g ml}^{-1}$	$2 \mu\text{g ml}^{-1}$	$1 \mu\text{g ml}^{-1}$	$2 \mu\text{g ml}^{-1}$	$1 \mu\text{g ml}^{-1}$	$2 \mu\text{g ml}^{-1}$
0	0.99+0.02 (-)	1.96+0.01 (-)	0.97+0.04 (-)	1.96+0.03 (-)	0.94+0.02 (-)	1.92+0.02 (-)
3	0.91+0.01 (8.08)	1.91+0.02 (2.55)	0.87+0.02 (9.66)	1.89+0.02 (3.24)	0.86+0.02 (9.18)	1.83+0.03 (4.85)
7	0.82+0.02 (16.84)	1.72+0.03 (12.56)	0.74+0.02 (23.11)	1.65+0.03 (15.67)	0.67+0.02 (28.62)	1.45+0.03 (24.44)
15	0.66+0.02 (33.67)	1.27+0.02 (35.48)	0.52+0.02 (45.87)	1.27+0.02 (35.26)	0.36+0.02 (61.49)	0.86+0.02 (55.11)
30	0.37+0.02 (62.29)	0.63+0.02 (68.08)	0.27+0.01 (72.07)	0.77+0.03 (60.82)	0.13+0.02 (85.87)	0.43+0.02 (77.64)
60	0.12+0.01 (87.88)	0.35+0.02 (82.00)	BDL	0.21+0.02 (89.27)	BDL	BDL
90	BDL	BDL	BDL	BDL	BDL	BDL
Regression Equation	Y=3.0184-0.0154X	Y=3.2962-0.0132X	Y=2.9948-0.0187X	Y=3.3286-0.0163X	Y=3.0055-0.0292X	Y=3.3049-0.0227X
Half-life ($T_{1/2}$) (days)	19.55	22.81	16.1	18.47	10.31	13.26

BDL: Below detectable limit of $0.10 \mu\text{g ml}^{-1}$; figures in parentheses denotes % dissipation

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