

# Kinetics and Hydrolysis of Fenamiphos, Fipronil, and Trifluralin in Aqueous Buffer Solutions

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Hydrolyses of fenamiphos, fipronil, and trifluralin were studied in aqueous buffer solutions of pH 4.1, 7.1, and 9.1 at different temperatures, 5,  $22 \pm 1$ ,  $32 \pm 1$ , and  $50 \pm 1$  °C. Fenamiphos, fipronil, and trifluralin were found to be more stable in acidic and neutral buffer solutions at temperatures of 5 and  $22 \pm 1$ , and dissipation is rapid at  $50 \pm 1$  °C. In basic buffer and at higher temperature, degradation of fenamiphos was found to be very rapid when compared with fipronil and trifluralin. The rate constants calculated at 32 °C for fenamiphos were  $2349.4 \times 10^{-8}$  (pH 4.1),  $225.2 \times 10^{-8}$  (pH 7.1), and  $30476.0 \times 10^{-8}$  (pH 9.1); for fipronil  $1750.0 \times 10^{-8}$  (pH 4.1),  $3103.0 \times 10^{-8}$  (pH 7.1), and  $3883.0 \times 10^{-8}$  (pH 9.1); and for trifluralin  $2331.0 \times 10^{-8}$  (pH 4.1),  $2360.0 \times 10^{-8}$  (pH 7.1), and  $3188.0 \times 10^{-8}$  (pH 9.1). On the basis of rate constant values, these pesticides appeared to be more susceptible to hydrolysis than synthetic organophosphorus compounds such as chlorpyrifos, diazinon, malathion, and ronnel. DT<sub>50</sub> values calculated at 32 °C were 228 (pH 4.1), 5310.24 (pH 7.1), and 37.68 (pH 9.1) h for fenamiphos; 608.6 (pH 4.1), 373.9 (pH 7.1), and 270.2 (pH 9.1) h for fipronil; and 502.1 (pH 4.1), 496.8 (pH 7.1), and 355.7 (pH 9.1) h for trifluralin.

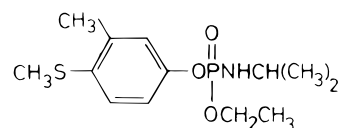
**Keywords:** Hydrolysis; aqueous buffer; fenamiphos; fipronil; trifluralin; kinetics

## INTRODUCTION

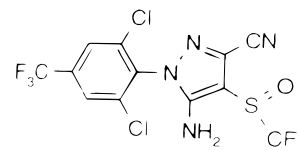
Pesticides are invaluable inputs for increased agricultural production. Improper usage of pesticides by farmers leads to environmental contamination (USEPA Guidance, 1966; Westlake and Gunther, 1966; Robinson, 1973; Krause and August, 1983; Barcelo et al., 1994; Lartiges and Garrigues, 1995; Vink and Vanderzee, 1996).

Since the discovery in the early 1980s of trace residues of pesticides in well water in many agricultural areas of the United States, there have been numerous reports of water contamination by these compounds in most countries where intensive agriculture is practiced (Walker et al., 1995). As the movement of water through the soil is the main principal mechanism for the pesticides to reach the surface and groundwater, there has been increased research interest aimed at understanding the process that controls the penetration of pesticides into the soil and their subsequent contamination of groundwater and surface water. Accumulation of these toxic pesticides in groundwater is influenced by the physical, chemical, and biological mechanisms. Thermal decomposition, pH variations in water, and hydrolysis have a major role in the breakdown and degradation of pesticides (Lee et al., 1986; Ou and Rao, 1986; Singh et al., 1990; Cavalier et al., 1991). Water, being a principal reactive agent of chemical degradation, is responsible for considerable breakdown of pesticide molecules and varies extensively with pH extremes. Even though the degradation of pesticides and their kinetics in aqueous solutions have been reported in the literature (Lee et al., 1986; Farber and Scholer, 1993; Hong and Pehkonen, 1998), not much work has been done in this direction.

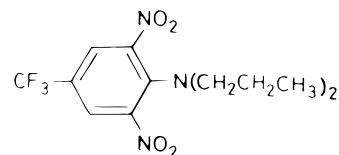
Detailed knowledge of the kinetics and hydrolysis pathways of pesticides is pertinent in designing experiments to obtain reliable rate constants for use in assessing the fate and transport of pesticide pollutants in aquatic ecosystems. In view of the importance of pesticide stability in the agro-ecosystem, the kinetics and hydrolysis of three different compounds belonging to three different groups fenamiphos (organophosphorus pesticide), fipronil (phenyl pyrazole compound), and trifluralin (2,6-dinitro aniline) at several pH and tem-



FENAMIPHOS



FIPRONIL



TRIFLURALIN

perature conditions were studied and the results presented in this paper.

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**Table 1. Recovery Details of Fenamiphos, Fipronil, and Trifluralin**

fenamiphos				fipronil				trifluralin			
added concentration	ppm found	rec %	RSD <sup>a</sup>	added concentration	ppm found	rec %	RSD <sup>a</sup>	added concentration	ppm found	rec %	RSD <sup>a</sup>
0.05	0.046–0.049	92–98	4.46	0.05	0.046–0.048	92–96	2.13	0.05	0.049–0.050	98–100	1.15
0.10	0.093–0.098	93–98	2.63	0.10	0.093–0.097	93–97	2.11	0.10	0.098–0.100	98–100	1.00
1.00	0.95–0.98	95–98	1.59	1.00	0.95–0.98	95–98	1.59	1.00	0.98–1.01	98–101	1.54

<sup>a</sup> Slope = 2.08 for fenamiphos, 2.02 for fipronil, and 0.55 for trifluralin. Correlation = 0.70 for fenamiphos, 0.92 for fipronil, and 0.89 for trifluralin. Coefficient intercept = 94.31 for fenamiphos, 94.34 for fipronil, and 98.79 for trifluralin. RSD, average of six determinations.

## MATERIALS AND METHODS

**Experimental.** A Nucon 5765 gas chromatograph equipped with <sup>63</sup>Ni ECD detector was used for the determination of fipronil and trifluralin residue. Fipronil was analyzed using a 2 m (length) × 1/4 in. (o.d.) glass column packed with Apiezon-M on a Chromosorb WAW DMCS 100–120 mesh column at an injector temperature of 250 °C, a detector temperature of 260 °C, and a column oven temperature of 210 °C. Nitrogen is used as a carrier gas with a flow rate of 1.75 kg/cm<sup>2</sup>. Trifluralin was analyzed using a 2 m (length) × 1/4 in. (o.d.) glass column packed with 5% SE-30 on a Chromosorb WHP 100–120 mesh column at a column oven temperature of 190 °C, an injector temperature of 250 °C, and a detector temperature of 280 °C. A 0.5 μL amount of sample was injected. The retention times for fipronil and trifluralin were 3.3 and 4.2 min, respectively.

Fenamiphos was analyzed using a Shimadzu (Tokyo, Japan) liquid chromatograph consisting of a LC-10 AT model pump and SPD-10A UV spectrophotometric detector. RP-18 Li-chrosorb (5 μm) 25 cm (length) × 4.6 mm (i.d.) column at a wavelength of 253 nm and an isocratic mobile phase (methanol:water (80:20)) were used in the studies. A 20 μL amount was injected by a 25 μL Hamilton syringe. Data were recorded using CLASS CR-10 software.

**Reagents.** Residue-grade acetonitrile, hexane, and HPLC-grade methanol were obtained from E. Merck (Darmstadt, Germany). Analar-grade potassium dihydrogen orthophosphate, boric acid, potassium chloride, sodium hydroxide, and dichloromethane were all obtained from Fischer Inorganics and Aromatics Limited (Chennai, India). The analytical reference standard of fenamiphos (91%) was purchased from Chemservice (West Chester, PA). The analytical reference standard of fipronil (98.7%) was obtained from Rhone-Poulenc Agrochemicals (India, New Delhi), and the trifluralin reference standard of known purity (99%) was obtained from Gharda Chemicals Limited (Dombivli, India).

**Preparation of Solutions.** A stock solution of reference standards of concentration 1000 μg/mL was prepared by dissolving 10 mg of fipronil in residue-grade acetonitrile, fenamiphos in HPLC-grade methanol, and trifluralin in residue-grade hexane. Working standards were prepared by diluting the stock solutions. All the solutions were stored in a freezer at –10 °C.

Different buffer solutions of pH 4.1, 7.1, and 9.1 were prepared in triple glass distilled water using appropriate reagents as described by Dawson et al. (1969).

**Sample Preparation.** *Fenamiphos.* A 25 mL sample of water was uniformly collected from each container on different occasions using a pipet, transferred into a separatory funnel with a capacity of about 250 mL, and partitioned 3 times with 50 mL of dichloromethane by vigorous shaking for 2 min. The organic layer was collected each time and dried over anhydrous sodium sulfate. This was concentrated to near dryness using a vacuum rotary evaporator and reconstituted in 3 mL of methanol.

*Fipronil.* A 25 mL water sample was partitioned with 75, 50, and 50 mL of hexane. The organic layer was collected each time and dried over anhydrous sodium sulfate. The residue sample was evaporated to near dryness and dissolved in acetonitrile for analysis.

*Trifluralin.* A 500 mg sample of graphitized carbon black, M/s. Indo National Ltd., India, was fitted in a 1 cm stainless

steel glass cartridge between two Teflon frits. The cartridge was connected to a solvent recovery flask through a vacuum pump and conditioned by rinsing with 10 mL of water and 2 mL of acetone.

A 25 mL water sample was transferred into the column and allowed to percolate for 5 min, and then a vacuum was applied to drain the water completely. The column was eluted with 10 mL of acetone slowly. The eluant was filtered and evaporated under vacuum and the residues reconstituted in acetone for quantitative analysis by gas chromatography.

**Recovery Studies.** Validation of the method was performed in terms of fortification and recovery studies. Each pesticide was fortified at different concentrations (1.0, 0.1, and 0.05 μg/mL) in 10 mL of buffer solutions. Samples were processed as mentioned earlier and analyzed. Mean analytical recoveries calculated for fenamiphos and fipronil were 95.1 and 95.11 with a RSD value of 1.59–4.46 and 1.59–2.13, respectively. Preconcentration of trifluralin is found to be highly effective on graphitized carbon black with a mean recovery of 99.00% for 18 successive determinations made, and the relative standard deviation is 1.00–1.54%. The minimum detectable level of the method (LOD) in gas chromatography and high-performance liquid chromatography was 0.001 μg/mL.

**Incubation of Fenamiphos, Fipronil, and Trifluralin in Aqueous Buffers.** Buffer solutions of pH 4.1, 7.1, and 9.1 were kept in a constant-temperature bath at 5, 22 ± 1, 32 ± 1, and 50 ± 1 °C. The required quantities of fenamiphos, fipronil, and trifluralin (20 mL of 100 μg/mL) were fortified into 1 L of different buffer solutions to give a uniform concentration of 2.0 μg/mL. Three replicates were prepared from each stock solution and stored under identical conditions. One control sample was also maintained for each pesticide at each buffer solution (unspiked solution). To determine the kinetics, all the samples were sealed and incubated.

## RESULTS AND DISCUSSION

Fenamiphos, an organophosphorus thioate insecticide, was selected to study in the aqueous phase because of its potential to hydrolyze not only in water but also in the bottom sediments. In general, alkaline hydrolysis of organophosphorus compounds is described by a second-order rate expression that is first order for ester and first order in hydroxyl ion activities (Cox and Ramsay, 1964), representing the plot of the log of the rate constant versus pH with a slope 1. In the case of fenamiphos, such a plot is nonlinear and at the higher pH levels alkaline hydrolysis dominates but the reaction does not obey second-order kinetics.

Hydrolysis of fenamiphos, fipronil, and trifluralin in the pH range 4.1–9.1 followed simple pseudo-first-order kinetics. Data observed at different pH and temperature gradients was presented in Tables 2–4. Significant variations can be observed in dissipation with respect to pH and temperature.

At 32 ± 1 °C, the initial concentration of 2.0 μg/mL fenamiphos is observed in acidic water; by sixtieth day the concentration went below the detectable level (<0.001 μg/mL). In the case of normal water, only 10–15% dissipation is observed, whereas in basic water of pH

**Table 2. Dissipation of Fenamiphos at 5, 22 ± 1, 32 ± 1, and 50 ± 1 °C in Aqueous Buffer Solutions**

occasion (days)	residue, µg/mL													
	5 °C			22 ± 1 °C			32 ± 1 °C			50 ± 1 °C				
	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 7.1	pH 4.1	pH 9.1		
0	2.045	1.985	1.992	2.054	1.998	1.983	2.011	2.190	0	1.912	2.006	0	1.989	1.984
10	2.040	1.984	1.987	2.023	1.995	1.975	1.624	2.120	1	1.294	1.821	76	1.642	0.415
20	2.035	1.983	1.982	1.994	1.990	1.967	1.232	2.040	3	0.635	1.663	151	1.276	<0.001
30	2.031	1.982	1.977	1.958	1.986	1.960	0.854	1.970	5	0.203	1.475	300	0.821	
40	2.026	1.981	1.971	1.923	1.982	1.952	0.432	1.900	7	<0.001	1.348	600	0.372	
60	2.016	1.980	1.961	1.874	1.976	1.939	0.020	1.825			1.217	900	<0.001	
											1200			

**Table 3. Dissipation of Fipronil at 5, 22 ± 1, 32 ± 1, and 50 ± 1 °C in Aqueous Buffer Solutions**

occasion (days)	residue µg/mL												
	5 °C			22 ± 1 °C			32 ± 1 °C			50 ± 1 °C			
	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	
0	1.965	1.973	1.956	1.958	1.972	1.968	1.915	1.942	2.008	0	1.936	1.951	1.967
10	1.960	1.970	1.950	1.950	1.961	1.954	1.713	1.433	1.534	3	1.438	1.325	1.008
20	1.964	1.968	1.943	1.944	1.951	1.939	1.454	1.051	1.034	7	1.015	0.878	0.562
30	1.947	1.961	1.934	1.934	1.939	1.925	0.998	0.827	0.854	10	0.532	0.433	0.046
40	1.940	1.953	1.927	1.923	1.929	1.912	0.754	0.279	0.320	15	0.118	0.082	<0.001
60	1.931	1.944	1.918	1.911	1.915	1.897	0.392	0.155	0.047				

**Table 4. Dissipation of Trifluralin at 5, 22 ± 1, 32 ± 1, and 50 ± 1 °C in Aqueous Buffer Solutions**

occasion (days)	residue µg/mL											
	5 °C			22 ± 1 °C			32 ± 1 °C			50 ± 1 °C		
	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1	pH 4.1	pH 7.1	pH 9.1
0	1.932	1.924	1.936	1.941	1.937	1.929	1.904	1.889	1.882	1.913	1.934	1.894
10	1.927	1.917	1.927	1.930	1.923	1.911	1.264	1.247	1.200	1.078	1.121	1.015
20	1.923	1.910	1.920	1.921	1.911	1.892	0.878	0.856	0.793	0.551	0.608	0.498
30	1.914	1.901	1.911	1.908	1.894	1.873	0.714	0.713	0.525	0.109	0.183	0.052
40	1.903	1.893	1.902	1.895	1.881	1.855	0.522	0.510	0.330	<0.001	0.042	<0.001
60	1.895	1.886	1.888	1.876	1.862	1.830	0.242	0.234	0.109			

9.1, faster dissipation of fenamiphos can be seen and the residues went below the detectable level by the third day. When studied, the hydrolysis at 22 ± 1 °C result shows that the reaction is very slow at this temperature. At the end of sixtieth day, only 8–9% dissipation from the initial concentration is observed in acidic water; dissipation is very slow (0.5–1%) in normal water and in basic water (1.5–2.0%) during the above study period. A further decrease in the temperature to 5 °C showed only 1–1.5% dissipation in both acidic and basic water and no change in the initial concentrations of neutral water. At 50 ± 1 °C, complete hydrolysis of the product is observed in basic water within 60 min; it took 8 h in acidic water. In the case of neutral water, only 40% dissipation of the initial concentration is observed.

No significant change is observed in the dissipation of fipronil at 5 °C in all the buffer solutions tested. At 22 ± 1 °C dissipation of fipronil is 2.4–3.6%. By the sixtieth day at 32 ± 1 °C, the initial concentration (2.0 µg/mL) reduced to 0.392 µg/mL (80%) in acidic buffer and in neutral buffer it reduced to 0.155 µg/mL (92%). In basic buffer, degradation is 98% on sixtieth day. At 50 ± 1 °C, complete dissipation of fipronil is observed by twentieth day in acidic and neutral buffer and by fifteenth day in basic buffer.

Dissipation of trifluralin on the sixtieth day at 5 °C is only 1.9–2.5%. At 22 ± 1 °C, trifluralin dissipation is in the range of 3.35–5.1%. At 32 ± 1 °C, hydrolysis

is about 87% in acidic and neutral buffer solutions within 60 days and in basic buffer it is nearly 95% at this time point. At 50 ± 1 °C, 98% of trifluralin dissipated within 40 days in neutral water whereas complete dissipation was observed in acidic and basic buffers.

To determine the kinetics of the degradation of fenamiphos, fipronil, and trifluralin, concentration versus time plots were constructed. On the basis of the dissipation data, the half-life values ( $DT_{50}$ ) were calculated by using the regression analysis and the rate constant  $k$  was calculated from the first-order rate equation.  $k$  values and  $t_{1/2}$  values are presented in Tables 5 and 6.

$C_t = C_0 e^{-kt}$  where  $C_t$  is the concentration of pesticide at time  $t$ ,  $C_0$  represents the initial concentration, and  $k$  is the rate constant  $dt = -k dc$ .

The rate constant  $k$  is also calculated from the dissipation of fenamiphos, fipronil, and trifluralin with time using the following equation

$$k = \ln C_1/C_2/\Delta t$$

where  $\Delta t$  is the time interval ( $t_1 - t_2$ ) and  $C_1$  and  $C_2$  are the concentrations of pesticides at times  $t_1$  and  $t_2$  respectively. In the present pH range of study 4.1–9.1, the rate of dissipation followed pseudo-first-order kinetics (Tables 5 and 6). The rate of hydrolysis varied with



**Table 5. Values of  $k$  (Rate Constant) Calculated From Hydrolysis Data**

name of the pesticide	$k$ ( $\text{h}^{-1}$ )				relative standard deviation			
	5 °C ( $\times 10^{-8}$ )	22 ± 1 °C ( $\times 10^{-8}$ )	32 ± 1 °C ( $\times 10^{-8}$ )	50 ± 1 °C ( $\times 10^{-8}$ )	5 °C	22 ± 1 °C	32 ± 1 °C	50 ± 1 °C
Acidic Buffer (4.1)								
fenamiphos	16.4	109.4	2349.4	442 758.0	9.2	14.8	61.3	34.6
fipronil	21.0	29.4	1750.0	7495.0	23.8	22.0	22.2	27.6
trifluralin	23.9	40.3	2331.0	6632.0	8.7	9.0	26.2	
Neutral Buffer (7.1)								
fenamiphos	3.15	13.27	225.2	623.1	19.3	27.9	39.4	72.0
fipronil	17.4	35.7	3103.0	13 894.0	52.2	18.2	71.8	52.7
trifluralin	25.1	47.8	2360.0	6649.0	24.3	23.0	61.2	94.0
Basic Buffer (9.1)								
fenamiphos	18.25	26.5	30 476.0	5 173 910.0	48.9	170.3	23.9	60.5
fipronil	24.0	45.6	3883.0	27 852.0	29.9	20.5	27.2	47.2
trifluralin	29.8	63.8	3188.0	8322	13.1	14.9	12.5	76.8

**Table 6.  $t_{1/2}$  (Half-Life) Calculated from Hydrolysis Data**

name of the pesticide	$t_{1/2}$ (h)			
	5 °C	22 ± 1 °C	32 ± 1 °C	50 ± 1 °C
Acidic Buffer (4.1)				
fenamiphos	70 580.40	10 651.00	228.00	2.64
fipronil	55 190.40	39 794.20	608.60	91.68
trifluralin	48 333.60	28 783.20	502.10	179.50
Neutral Buffer (7.1)				
fenamiphos	384 749.80	87 313.40	5310.20	1929.12
fipronil	63 895.20	33 367.20	373.90	81.12
trifluralin	47 793.60	24 703.20	496.80	175.70
Basic Buffer (9.1)				
fenamiphos	63 230.40	44 334.00	37.68	0.24
fipronil	48 815.50	26 488.60	270.20	48.48
trifluralin	39 470.40	18 567.10	355.70	144.70

respect to pH, being more rapid at a basic than at an acidic pH at 32 °C; the trend became equal at lower temperature, 5 °C.

Hydrolysis susceptibilities of fenamiphos, fipronil, and trifluralin were compared with that of synthetic organophosphate insecticides chlorpyrifos, diazinon, malathion, parathion, and ronnel as reported in the literature (Gomaa and Faust, 1972; Wolfe et al. 1983; Macalady and Wolfe, 1983). The rate of hydrolysis of fenamiphos, fipronil, and trifluralin at 32 °C (pH 7.1) was  $0.023 \times 10^{-4}$ ,  $0.31 \times 10^{-4}$ , and  $0.24 \times 10^{-4} \text{ h}^{-1}$  which is less than diazinon ( $(7.2 \pm 1.2) \times 10^{-4} \text{ h}^{-1}$ ) and ronnel ( $(1.2 \pm 0.1) \times 10^{-3} \text{ h}^{-1}$ ).

At 22 ± 1 °C and pH 4.1, the rate of hydrolysis of fenamiphos, fipronil, and trifluralin is  $0.11 \times 10^{-5}$ ,  $0.03 \times 10^{-5}$ , and  $0.04 \times 10^{-5} \text{ h}^{-1}$  whereas chlorpyrifos under identical conditions showed  $37 \times 10^{-5} \text{ h}^{-1}$ . At 50 ± 1 °C, fenamiphos had a rate of hydrolysis almost 1–2 orders of magnitude higher than that of diazinon, ronnel, and chlorpyrifos (pH 4.1,  $4.42 \times 10^{-3} \text{ h}^{-1}$ ; pH 9.1,  $51.7 \times 10^{-3} \text{ h}^{-1}$ ). Further, the rate of hydrolysis of fenamiphos at pH 7.1 ( $0.0062 \times 10^{-3} \text{ h}^{-1}$ ) is lower when compared with pH 4.1 and 9.1 at this temperature, and the rate of hydrolysis of fipronil and trifluralin is relatively slow when compared with fenamiphos [fipronil:  $0.75 \times 10^{-4} \text{ h}^{-1}$  (pH 4.1);  $1.39 \times 10^{-4} \text{ h}^{-1}$  (pH 7.1);  $2.79 \times 10^{-4} \text{ h}^{-1}$  (pH 9.1); trifluralin:  $0.66 \times 10^{-4} \text{ h}^{-1}$  (pH 4.1);  $0.66 \times 10^{-4} \text{ h}^{-1}$  (pH 7.1);  $0.83 \times 10^{-4} \text{ h}^{-1}$  (pH 9.1)].

The calculated half-life values at 50 ± 1 °C for fenamiphos are 2.64 h (pH 4.1) 1929.12 h (pH 7.1), and 0.24 h (pH 9.1). For fipronil 91.68 h (pH 4.1), 81.12 h (pH 7.1) and 48.48 h (pH 9.1) and for trifluralin 179.5 h (pH 4.1), 175.7 h (pH 7.1), and 144.7 h (pH 9.1). From the hydrolysis and half-life values, it is inferred that degradation of fenamiphos, fipronil, and trifluralin was rapid and had a pseudo-first-order at of 50 ± 1 °C.

Taking into account the fact that the pH was constant with time, the observed first-order kinetics for the reaction agree with the mechanisms proposed by Katagi (1993). The pH value measured at the end of the hydrolysis did not show any variation from the initial value. Hence, the degradation can be attributed to the presence of hydroxyl ion concentration in strong alkaline medium and the reaction occurred instantaneously. However, in fenamiphos in neutral conditions, complete hydrolysis did not occur. Fenamiphos initially showed some decay and later was almost constant. This can be attributed to the possible reversible nature, as reported in the case of ethiofencarb by Jesus Sans-Asensio (1997). This phenomenon was mainly observed at lower temperatures. No equilibrium was observed at 32 ± 1 and 50 ± 1 °C. The variations observed in the case of acidic water may be due to the influence of metal ion catalysis. In the case of fipronil and trifluralin, uniformity in hydrolysis with an increase in hydroxyl ion concentration is observed, which is in agreement with the Katagi model.

## CONCLUSION

From the above results it can be concluded that the presence of ionic substances alters the hydrolysis mechanism of fenamiphos, fipronil and trifluralin. The more alkaline the soil, the faster the hydrolysis. However, the soils of a neutral nature favor the accumulation of residues of these pesticides for a longer time, which may contribute to groundwater pollution.

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## LITERATURE CITED

- Barcelo, D.; House, W. A.; Maier, E. A.; Griepink, B. Preparation, Homogeneity and stability studies of freeze-dried water containing pesticides. *Int. J. Environ. Anal. Chem.* **1994**, *57*, 237–54.
- Blanchet, P. F.; George, A. Kinetics of chemical degradation of Organophosphorous pesticides. Hydrolysis of chlorpyrifos and chlorpyrifos methyl in the presence of copper(II). *Pestic. Sci.* **1982**, *13*, 85–89.
- Cavalier, T. C.; Lavy, T. L.; Mattice, J. D. Persistence of selected pesticides in groundwater samples. *Groundwater* **1991**, *29*, 225–31.

- Cox, J. R., Jr.; Ramsay, B. *Chem. Rev.* **1964**, *64*, 317.
- Dawson, R. M. C.; Elliott, W. H.; Jones, K. M. *Data for Biochemical Research*, 2nd ed.; Clarendon Press: Oxford, U.K., 1969; pp 483–504.
- Farber, H.; Scholer, H. F. GC determination of carbamate pesticides after flash-heater methylation with trimethyl sulfonium hydroxide. *J. Agric. Food Chem.* **1993**, *41*, 217–20.
- Gomaa, H. M.; Faust, S. D. Chemical hydrolysis and oxidation of parathion and paraoxon in aquatic environment. In *Fate of Organic Pesticides in the Aquatic Environment*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1972; p 189.
- Hong, F.; Pehkonen, S. Hydrolysis of phorate using simulated environmental conditions: Rates, Mechanisms and product analysis. *J. Agric. Food Chem.* **1998**, *46*, 1192–1199.
- Katagi, T. In *Rational approaches to structure, activity and ecotoxicology of agrochemicals*; 1993; Vol. 33, pp 310–19.
- Krause, R. T.; August, M. E. Applicability of a multiresidue method and high performance liquid chromatography for determining quinomethionate in apples and oranges. *J. Assoc. Anal. Chem.* **1983**, *66*, 234–237.
- Lartiges, S. B.; Garrigues, P. P. Degradation Kinetics of Organophosphorous and Organonitrogen Pesticides in different water under various Environmental conditions. *Environ. Sci. Technol.* **1995**, *29*, 1246–54.
- Lee, Ch. Ch.; Green, R. E.; Apt, W. J. Transformation and adsorption of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in molokai soil and simulated movement with irrigation. *J. Contam. Hydrol.* **1986**, *1*, 211–225.
- Macalady, D. L.; Wolfe, N. L. New perspectives on the hydrolytic degradation of the organophosphorothioate insecticide chlorpyrifos. *J. Agric. Food Chem.* **1983**, *31*, 1139–47.
- Ou, L. T.; Rao, P. S. C. Degradation and metabolism of oxamyl and phenamiphos in soils. *J. Environ. Sci. Health* **1986**, *B21*, 25–33.
- Perdue, E. M.; Wolfe, N. L. Prediction of buffer catalysis in field and laboratory studies of pollutant hydrolysis reactions. *Environ. Sci. Toxicol.* **1983**, *17*, 635–642.
- Robinson, J. Dynamics of Pesticide Residue in the Environment in *Environmental Pollution by Pesticides*; Edwards, C. A., Ed.; Plenum Press: London, 1973.
- Sanz-Asensio, J.; Plaza-Medina, M.; Martinez-Soria, M. T. Kinetic study of the degradation of Ethiofencarb in Aqueous solutions. *Pestic. Sci.* **1997**, *50*, 187–94.
- Singh, R. P.; Brindle, I. D.; Hall, C. D.; Chiba, M. Kinetic study of the decomposition of methyl [1-(butylcarbamoyl)-1H-benzimidazol-2-yl] carbamate (benomyl) to methyl-1H-benzimidazol-2-yl carbamate (MBC). *J. Agric. Food Chem.* **1990**, *38*, 1758–62.
- U.S. Environmental Protection Agency Guidance for conducting Remedial Investigations and feasibility studies under CERCLA, Interim Final EPA/540/G-89/004, Washington, DC, 1989.
- Vink, J. P. M.; Vanderzee, S. E. A. T. M. Some Physicochemical and environmental factors affecting transformation rates and sorption of the herbicide of the metamiltron in soil. *Pestic. Sci.* **1996**, *46*, 113–19.
- Walker, A.; Allen, R.; Bailey, S. W.; Blair, A. M.; Brown, C. D.; Gunther, P.; Leake, C. R.; Nicholls, P. H. *Pesticide movement to water*; Monograph 62; BCPC: Surrey, U.K., 1995.
- Westlake, W. E.; Gunther, F. A. Occurrence and mode of Introduction of pesticides in the Environment In *organic pesticides in the environment*; Advances in Chemistry Series 60; American Chemical Society: Washington, DC, 1966; p 110.

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