

Effect of pH and Type of Formulation on the Persistence of Imidacloprid in Water

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Imidacloprid [1-[(6-Chloro-3-Pyridinyl) methyl]- N-nitro -2- Imidazolidinimine] is a newly introduced broad spectrum systemic insecticide in the Indian sub-continent by M/s. Bayer India Ltd.. This new chloronicotinyl compound is fairly soluble in water as compared to other non-polar insecticides (Kagabu 1997). It is effective against sucking insects, soil insects, termites and some species of chewing insects and is used as seed dressing, soil treatments and foliar treatment in different crop (Tomlin 1994). Some information regarding the fate of imidacloprid in soil are available (Cox *et al.* 1997; Rouchaud *et al.* 1994; 1996). Photolysis of the insecticide in aqueous solution was reported by Moza *et al.* (1998). But little is known about its persistence behaviour in water. The objective of the present investigation is to evaluate the effect of pH of water as well as the type of formulations on the persistence behaviour of imidacloprid in aqueous solution.

MATERIALS AND METHODS

Analytical grade imidacloprid (purity 99%) and its two formulations - Confidor 200 SL and Gaucho 70 WS were obtained from Ms. Bayer India Ltd.. The reagents used were of analytical grade and the solvents were HPLC grade.

The buffer solutions (Titrisol of pH - 4.0, 7.0 and 9.0, E. Merck India Ltd.) were added @ 50mL/500mL of water (HPLC grade) and are designated as A, B and C respectively. 100 ml of these buffered solutions were taken in amber colored glass bottles. Confidor 200 SL (0.5 g) was dissolved in 1.0 L of water (100 µg/mL a.i.) and suitably diluted to 1.0 µg/mL of imidacloprid in the final solution. From this stock solution, Confidor 200 SL (imidacloprid) was applied @ 0.078 mg/L a.i. (T_1) and 0.155 mg/L a.i. (T_2) in different batches of water (A, B, C) in three replicate numbers. Seven such sets were prepared for sampling at 0, 7, 15, 20, 30, 45 and 60 d after application of the pesticide. All the bottles were kept under room temperature ($30 \pm 5^\circ\text{C}$). Solution of Gaucho 70 WS (0.5 g/L) was also prepared (350 µg / mL a.i.) in the same manner, diluted to 1.0 µg/mL of imidacloprid and was applied to different sets of water as described above.

Water samples (100 mL) were extracted with dichloromethane (100 + 50 + 50 mL) using a separatory funnel after adding 10% sodium chloride solution (10 mL). The organic layer was collected over anhydrous sodium sulphate and concentrated by a rotary vacuum evaporator. The concentrated material was dissolved in acetonitrile for analysis. Imidacloprid residue was estimated by HPLC (Hewlett Packard model 1050) equipped with a UV variable detector coupled with a HP – 3395 integrator. The spherisorb reverse phase C-18 column (cartridge column) was used with 15 cm length and id 4.6 mm.

In order to evaluate the efficiency and reliability of the procedure adopted, recovery study was carried out by fortifying water with imidacloprid formulations. The mean recovery was found to be 90 - 91.5% for Confidor 200 SL and 89 - 89.2% for Gaucho 70 WS.

RESULTS AND DISCUSSION

The results of imidacloprid residues occurring in water (maintained at different pH) at different days are presented in Table 1 and Table 2. The initial concentration of the residues was found to vary from 0.049 - 0.075 µg/mL for the lower dose and 0.112 - 0.156 µg/mL for the higher dose at different pH of water irrespective of the type of formulations. After 60 d of application the residue remaining in water was found in the range of 0.009 - 0.014 µg/mL for T₁ or T₃ (Table 1) and 0.019 - 0.032 µg/mL for T₂ or T₄ (Table 2) doses of the different formulations used.

Table 1. Persistence of imidacloprid in water when applied @ 0.078 µg/mL.

Formulation	pH	Concentration* remaining in water (µg/mL) at different d						
		0	7	15	20	30	45	60
Confidor 200 SL (T ₁)	4.0	0.049	0.036	0.032	0.026	0.019	0.012	0.009
	7.0	0.061	0.052	0.042	0.033	0.026	0.018	0.011
	9.0	0.074	0.061	0.051	0.041	0.038	0.027	0.012
Gaucho 70 WS (T ₃)	4.0	0.050	0.037	0.033	0.027	0.020	0.014	0.010
	7.0	0.063	0.054	0.043	0.035	0.028	0.020	0.010
	9.0	0.075	0.064	0.053	0.044	0.039	0.029	0.014

*average of three replications

The percentage dissipation of imidacloprid with time is presented in Fig. 1 and Fig. 2. The initial concentration dissipated to 17-35% within 15 d. The dissipation increased to 45-62% in 30 d and 79-86% in 60 d for confidor 200 SL (Fig 1). In case of Gaucho 70 WS, the initial concentration dissipated to 21-34% within 15 d, 47-63 % in 30 d and 79-84% in 60 d (Fig.2). Dissipation followed the first order kinetics, as the log values of the residues produced straight line against time. The regression equations obtained are presented in Table 3 along with the calculated half- life values.

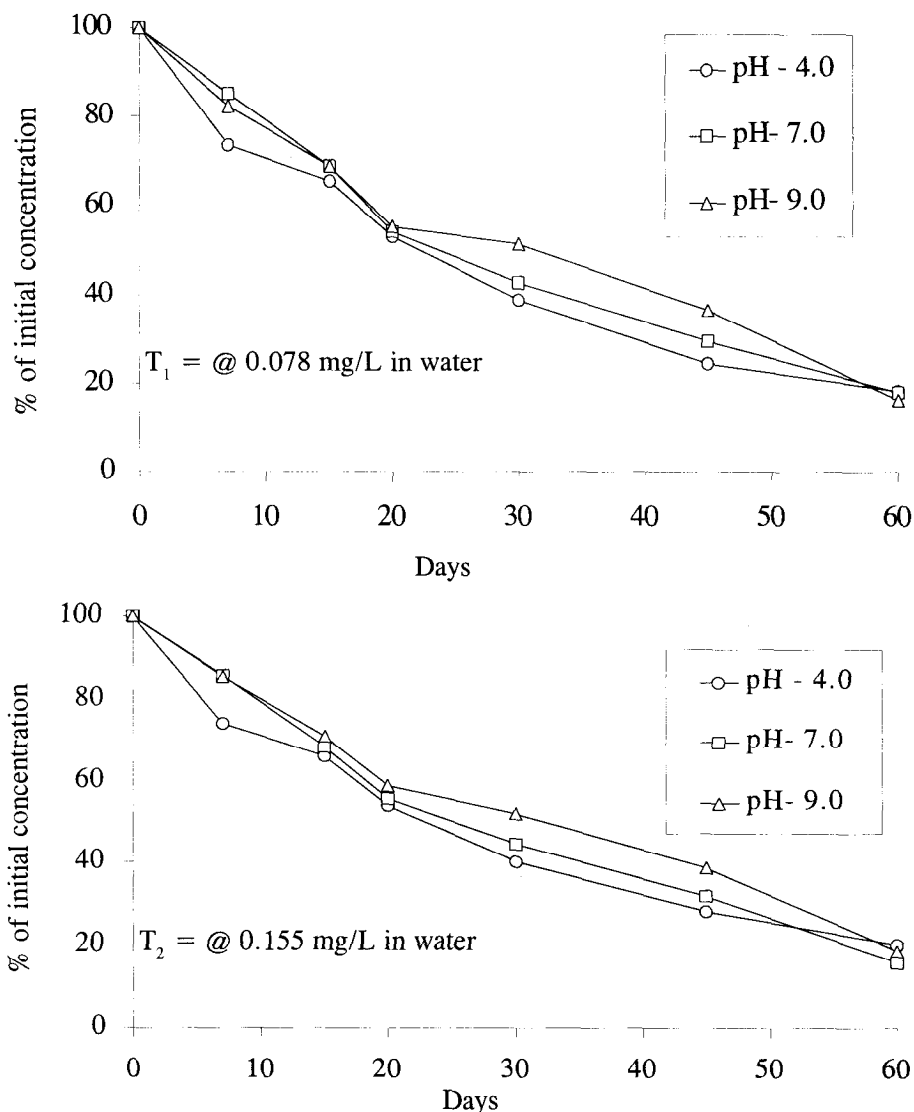


Figure 1. Dissipation of imidacloprid (Confidor 200 SL) in water

The persistence of imidacloprid in water increased with the increase of application rate. The calculated half-life values ranged from 31.0 - 36.3 d in T_1 , and 38.1 - 43.6 d in T_2 for the liquid formulation while for the powder formulation the corresponding values ranged from 34.5 - 40.1 d (T_1) and 41.2 - 46.3 (T_2). An increasing trend in the half-life values was also observed with the increase in pH of the aqueous media in all the treatment doses for both the formulations.

The persistence behaviour of imidacloprid was also influenced by the type of formulations. Higher half-life values were found in powder formulation as compared

Table 2. Persistence of imidacloprid in water when applied @ 0.155 µg / mL

Formulation	pH	Concentration* remaining in water (µg/mL) at different d						
		0	7	15	20	30	45	60
Confidor 200SL (T ₂)	4.0	0.133	0.121	0.100	0.072	0.061	0.051	0.019
	7.0	0.112	0.102	0.092	0.072	0.061	0.047	0.019
	9.0	0.152	0.139	0.119	0.082	0.065	0.038	0.031
Gaucho 70 WS (T ₄)	4.0	0.156	0.136	0.108	0.081	0.058	0.047	0.025
	7.0	0.153	0.140	0.120	0.086	0.065	0.039	0.032
	9.0	0.146	0.123	0.112	0.092	0.076	0.051	0.028

* average of three replications

to those obtained for the liquid formulation (Table - 3). The variations observed in observed in the persistence behaviour of imidacloprid due to rate of application, pH of water and type of formulation were statistically significant at 5% level (Table 4).

The mean half-life value was found to be the highest (41.6 d) at pH 9.0, indicating a longer persistence of the insecticide residues under alkaline condition. The lowest mean half-life value (36.2 d) was obtained under acidic condition. The effect of the formulation type on the persistence behaviour of imidacloprid in water was also significant. Higher persistence was observed with the powder formulation (mean $t_{1/2}$ =37.4 and 43.9 d) as compared to the liquid formulation (mean $t_{1/2}$ =33.7 and 41.0 d)

Table 3. Statistical interpretation of the residual data

Formulation	Dose	pH	Half life ($t_{1/2}$) (d)	Regression equation
Confidor 200 SL	T ₁	4.0	31.03	Y= 1.69 – 0.0097 X
		7.0	33.82	Y= 1.82 – 0.0089 X
		9.0	36.27	Y= 1.92 – 0.0083 X
	T ₂	4.0	38.10	Y= 2.25 – 0.0079 X
		7.0	41.20	Y= 2.14 – 0.0073 X
		9.0	43.60	Y= 2.23 – 0.0069 X
Gaucho 70 WS	T ₃	4.0	34.50	Y= 1.69 – 0.0087 X
		7.0	37.60	Y= 1.84 – 0.0080 X
		9.0	40.13	Y= 1.92 – 0.0075 X
	T ₄	4.0	41.20	Y= 2.23 – 0.0073 X
		7.0	44.26	Y= 2.23 – 0.0068 X
		9.0	46.31	Y= 2.21 – 0.0065 X

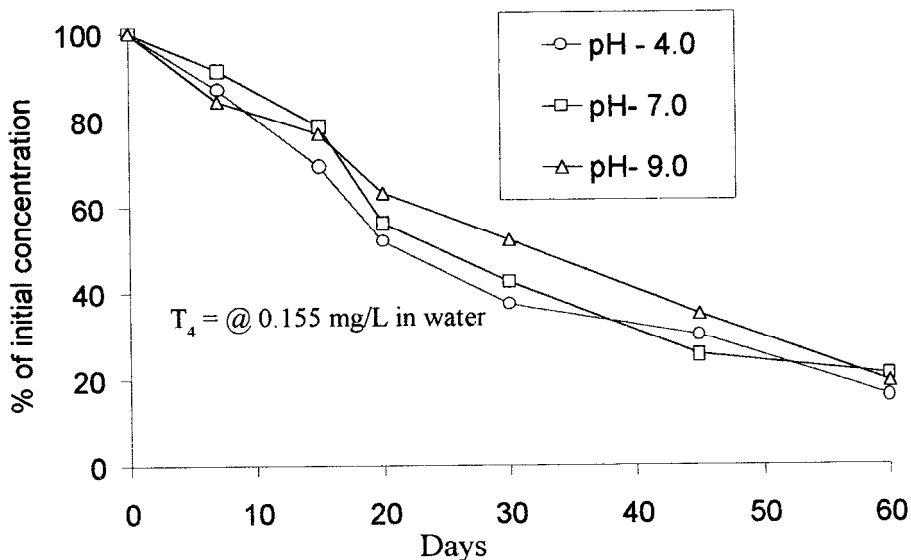
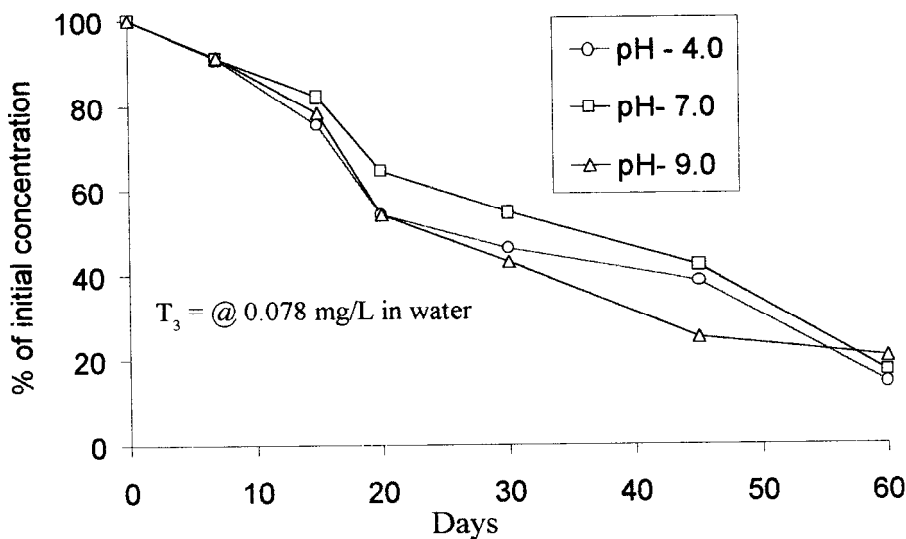


Figure 2 . Dissipation of imidacloprid (Gaucho 70 WS) in water

for both the doses (Table 4). It may be mentioned that such a trend was earlier reported for the persistence of granular and EC formulations of chlorpyrifos in soil (Chapman and Chapman 1986).

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Table 4. Effect of formulation, dose and pH on the persistence of imidacloprid

pH	Half-life value (d) of imidacloprid for different doses				Mean
	Confidor 200 SL		Gaucho 70 WS		
	T ₁	T ₂	T ₃	T ₄	
4.0	31.03	38.10	34.50	41.20	36.21
7.0	33.82	41.20	37.60	44.26	39.22
9.0	36.27	43.60	40.13	46.31	41.58
Mean	33.71	40.97	37.41	43.92	39.00
SEm (±) CD (0.05)	Dose		pH	Interaction	
	0.68		1.13	2.26	
	2.36		3.58	Not significant	

REFERENCES

- Chapman RA, Chapman PC (1986) Persistence of granular and EC formulations of chlorpyrifos in a mineral and an organic soil incubated in open and closed containers. *J. Environ. Sci. Health. B21* : 447-456
- Cox L, Koskinen WC, Yen PY (1997) Sorption-desorption of imidacloprid and its metabolites in soils. *J. Agric. Food Chem.* 45 : 1468-1472
- Kagabu S (1997) Chloronicotinyl insecticides-discovery, application and future perspective. *Rev. Toxicol.* 1: 75-129
- Moza PN, Hustert K, Feicht E, Kettrup A (1998) Photolysis of imidacloprid in aqueous solution. *Chemosphere* 36 : 497-502
- Rouchaud J, Gustin F, Wauters A (1994) Soil bio-degradation and leaf transfer of insecticide imidacloprid applied in seed dressing in sugar beet crops. *Bull. Environ. Contam. Toxicol.* 53 : 344-350
- Rouchaud J, Gustin F, Wauters A (1996) Imidacloprid insecticide soil metabolism in sugar beet field crops. *Bull. Environ. Contam. Toxicol.* 56 : 29-36
- Tomlin C (1994) *The pesticide manual*; British Crop Protection Council, Surrey, U.K., The Royal Society of Chemistry, Cambridge, U.K.