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The fate and behavior of *Imidacloprid 0.3% G* in water maintained at different pH and soils of different agro-climatic zones

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ABSTRACT

Imidacloprid 0.3% G is a new insecticide formulation having Imidacloprid [1-(6-chloro-3 pyridylmethyl) – N – nitroimida-zolidinimine] as active ingredient. A laboratory experiment was undertaken to determine the dissipation pattern as well as residue level of Imidacloprid 0.3% G exist in water maintained at different pH and soils of different agro-climatic zones following application at 1 ppm and 2 ppm. Samples were processed for analysis of Imidacloprid residues at intervals of 0 (2h after application), 5, 15, 30, 60 and 90 days after application. Imidacloprid 0.3% G was extracted from water by partitioning with dichloromethane. In case of soil samples the residue was extracted with acetonitrile: water (8:2) mixture. The extracts in acetonitrile were concentrated in rotary vacuum evaporator. The concentrated extract was subjected to solvent partitioning with dichloromethane. In both the cases, dichloromethane part after collection was evaporated to dryness in rotary vacuum evaporator. Final volume was reconstituted with acetonitrile for HPLC analysis. The residue of Imidacloprid 0.3% G in spiked water samples of pH 4.0, 7.0 and 9.2 as well as soils of different agro-climatic zones gradually decreased with time following first order kinetics in all the cases. The calculated half life ($T_{1/2}$) values in water were found to be in the range of 66.9 to 94.07 days and in case of different soils these values were range of 59.03-75.26 days. The dissipation of Imidacloprid 0.3% G appeared to be faster in acid medium than neutral but slower in alkaline medium.

Key Words: Behaviour, dissipation, fate and imidacloprid

Imidacloprid 0.3% G is a new insecticide formulation having Imidacloprid as active ingredient. Imidacloprid [1-(6-chloro-3 pyridylmethyl) –N–nitroimida-zolidinimine] is a 'chloronicotinyl' group of insecticide having systemic, contact and stomach action. Imidacloprid, first introduced by Bayer, was very effective against resistant pests due to acting as an agonist of the nicotinyl acetylcholine receptor (Chalan and Subbratnam, 1999, Olsen *et al*., 1996, Elbert and Nauen, 1996). It shows a high activity, especially against a sucking insects such as aphids, leaf and plant hoppers, thrips, whiteflies, soil insects, termites and some species of chewing insects as well as seed dressing, soil treatments and foliar treatments in different crops (Jarande *et al*., 1994, Kumar and Santharam, 1999, Kumar *et al*., 2001, Mote *et al*., 1994, Sarkar *et al*., 2001, Tomlin, 2000, Kanrar *et al*., 2006). The present investigation was undertaken to determine the dissipation pattern as well as residue level of Imidacloprid 0.3% G (very recently introduced by M/S Excel crop care Ltd., Mumbai) in water maintained at different pH and soils of different agro-climatic zones of India under the laboratory simulated condition at Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, West Bengal, India.

MATERIALS AND METHODS

1. Sample preparation

1.1 Preparation of water sample with varied pH level

One buffer capsule of pH 4.0, 7.0 and 9.2 per 100 ml of distilled water was used for preparation of water samples of the particular pH respectively. 200 ml distilled water was taken in each of a series of 250 ml conical flask and two buffer capsules were added to each of the conical flask. They were then left at room temperature for overnight for homogeneous mixing. The pH of water samples were checked intermittently during the entire study period.

1.2 Preparation of soil sample

Four types of agricultural field soils were collected from different agro-climatic zones, viz. i) New Alluvial soil from University Research Station, BCKV, Mohanpur, Nadia ii) Red and Lateritic soil from Regional Research Station, BCKV, Jhargram, Midnapore; and iii) Coastal Saline soil from Research Station of Central Soil Salinity Research Institute (ICAR) at Canning, 24- Parganas (S) iv) Black Soil from NRC Grapes, Pune, following the standard methodology of soil sampling. Soils were air dried, grinded and passed through 2 mm sieve and subsampled by the usual method of quartering. Selected physico-chemical properties of the soil are given in the Table 1. Soil texture was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was measured in soil + deionised water (1+2.5 by weight) (Jackson, 1973). The organic carbon content of the soil was determined by Walkley and Black wet oxidation method (Nelson and Soemmers, 1982).

2. Fortification of samples with Imidacloprid 0.3% G

2.1 Water sample

2 ml and 4 ml from the 100 ppm stock solutions of Imidacloprid 0.3% G were added to each

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conical flask containing 200 ml water of different pH. The initial concentrations become 1 ppm (T_1) and 2 ppm (T_2) respectively. For each treatment three replications were taken along with untreated control containing buffer solution.

2.2 Soil sample

Soil samples (50 g) were taken in 250 ml conical flasks to form a set for each type of soil and 10 ml of water was added to it. Then 1 ml and 2 ml of the 50 ppm stock solution of Imidacloprid were added to conical flasks separately containing 50 g of different soil samples. The initial concentrations become 1 ppm (T_1) and 2 ppm (T_2) respectively. The control soils (50 g) received 10 ml of water only. Three replicate flasks for each treatment were taken for analysis on each days of sampling along with untreated control. Samples (three replicates) were processed for analysis of Imidacloprid residues at intervals of 0 (2h after application), 5, 15, 30, 60 and 90 days after application.

2. 3 Extraction and clean up

2.3.1 Extraction and clean up of water samples

Water sample (200 ml) after addition of 10 g NaCl, was taken in a 1 l separatory funnel and partitioned thrice with dichloromethane (100 + 50 + 50 ml). Organic phase was collected over anhydrous Na_2SO_4. The combined dichloromethane fraction was evaporated to dryness in a rotary vacuum evaporator at 40^0C using water suction. Final volume was reconstituted with HPLC grade acetonitrile.

2.3.2 Extraction and clean up of soil samples

Soil sample (50 g) was taken in a 250 ml conical flask and 150 ml Acetonitrile : water (8:2) mixture was added to it and kept overnight. Then the conical flasks were shaken with a mechanical shaker for 2 hours and subsequently filtered. The acetonitrile extract obtained from soil sample was concentrated in rotary vacuum evaporator at 40^0C. After addition of 150 ml of distilled water and 10 g of NaCl the concentrated extract was subjected to solvent partitioning with dichloromethane for three times (100 + 50 + 50 ml). The dichloromethane fractions were collected through anhydrous sodium sulfate and concentrated to about 5 ml using rotary vacuum evaporator. The concentrated dichloromethane fraction was quantitatively transferred on a glass column packed with a mixture of 10 g of silica gel and 1 g of activated charcoal. 150 ml of dichloromethane was used as mobile phase to elute the residues of Imidacloprid. The cleaned up extract was collected and concentrated in rotary vacuum evaporator and finally the volume was reconstituted with HPLC grade acetonitrile.

2.4 Analysis of imidacloprid by HPLC

Imidacloprid was estimated by HPLC (Hewlett-Packard - Model 1050) equipped with Variable Wavelength detector (Agilent 1100 series) and Agilent 1100 series software. Reverse Phase C_{18} column (250 x 4.6 mm; Thermo Hypersil ODS, 5 μ) was used for chromatographic separation with Acetonitrile: Water (9:1 for water and 7:3 for soil samples) as the mobile phase at a flow rate of 1 ml min^{-1}. Under these working conditions imidacloprid was detected (at λ_{max} = 270 nm) with the retention times of 2.8 and 3.1 min for water and soil samples respectively. The LOD and LOQ of the method were 0.01 ppm and 0.05 ppm respectively for both soil and water.

2.5 Recovery study

Recovery study was carried out in control samples (with no previous history of imidacloprid application) in order to establish the efficiency and reliability of the analytical method employed.

2.5.1 Recovery study for water samples

Distilled water samples (200 ml), maintained at pH 4.0, 7.0 and 9.2 levels, were fortified at the level of 0.05, 0.1 and 1.0 ppm with the standard solutions of Imidacloprid and were analysed as mentioned in 2.4. The average recovery was in the range of 91.67 to 96.67 % (Table 2).

2.5.2 Recovery study for soil samples

Soil samples (50 g) were fortified at the level of 0.05, 0.1 and 1.0 ppm with the stock solutions of Imidacloprid and were analysed following the method as mentioned in 2.4. The average recovery was in the range of 92.67 to 99.00% (Table 3).

RESULTS AND DISCUSSION

The results regarding the residue of Imidacloprid 0.3% G in spiked water samples of pH 4.0, 7.0 and 9.2 as well as soils of different agro-climatic zones are summarized in Tables 4 and 5. No residue was detected in the control samples during the entire study. The residue gradually decreased with time following first order kinetics in all the cases. The calculated half life ($T_{1/2}$) values in water were found to be in the range of 66.9 to 70.01days, 81.36 to 88.54 days and 79.22 to 94.07 days in case pH 4.0, 7.0 and 9.2 respectively. In case of different soils these values were 59.03 days, 71.67 to 73.42 days 64.05 to 75.26 days and 66.9 to 71.67 days for Jhargram soil, Mohanpur soil, Canning soil and Pune soil respectively. In both the case Imidacloprid dissipated faster in acidic medium. The dissipation of Imidacloprid 0.3% G appeared to be faster in acid medium [*i.e.* in acidic water (pH 4.0) as well as in acidic soil (Jhargram soil)] than neutral but slower in alkaline medium. The result of present experiment is in well agreement with the result of the experiment entitled “Persistence and metabolism of imidacloprid in different soils of West Bengal” obtained by Sarkar *et al*., 2001.

Table 1: Physico-chemical properties of different soils

Location	Texture	pH	Bulk density (g/cm^3)	Organic carbon (%)
Jhargram	Sandy	5.56	1.58	0.52
Mohanpur	Sandy loam	6.85	1.28	0.76
Canning	Silty loam	7.92	1.45	1.21
Pune	Clayey	8.14	1.60	0.67

Table 2: Recovery study of imidacloprid in waters of different pH

Substrate	Amount fortified (ppm)	Amount recovered* (ppm)	Recovery (%)	Average recovery (%)
Acidic water (pH = 4.0)	0.05	0.04	80	
	0.1	0.09	90	91.67
	1.0	1.05	105	
Neutral water (pH = 7.0)	0.05	0.05	100	
	0.1	0.09	90	96.67
	1.0	1.00	100	
Alkaline water (pH = 9.2)	0.05	0.05	100	
	0.1	0.08	80	92.67
	1.0	0.98	98.0	

Table 3: Recovery study of imidacloprid in different soils

Substrate	Amount fortified (ppm)	Amount recovered* (ppm)	Recovery (%)	Average recovery (%)
	0.05	0.05	100.0	
Jhargram soil	0.1	0.09	90.0	91.67
	1.0	0.95	95.00	
	0.05	0.04	80.0	
Mohanpur soil	0.1	0.09	90.0	92.67
	1.0	1.08	108.0	
	0.05	0.40	80.0	
Canning soil	0.1	0.1	100.0	95.00
	1.0	1.05	105.0	
	0.05	0.05	100.0	
Pune soil	0.1	0.09	90.0	99.00
	1.0	1.07	107.0	

- Average of three replicates

Table 4: Dissipation of imidacloprid in different water

Water	Dose	Concentration remaining in soil (µg/ml) (±S.D) on day						$T_{1/2}$ (Days)	Regression equation
		0	5	15	30	60	90		
Acidic water (pH-4.0)	T_1	1.00± 0.01	0.90± 0.07	0.79± 0.02	0.61± 0.02	0.49± 0.00	0.39± 0.01	66.9	y = -0.0045x + 2.9682
	T_2	1.99± 0.01	1.86± 0.05	1.63± 0.04	1.19± 0.02	1.01± 0.01	0.82± 0.002	70.01	y = -0.0043x + 3.2719
Neutral Water (pH 7.0)	T_1	0.96± 0.02	0.90± 0.02	0.79± 0.02	0.67± 0.04	0.53± 0.01	0.45± 0.04	81.36	y = -0.0037x + 2.9618
	T_2	1.95± 0.01	1.86± 0.05	1.65± 0.05	1.31± 0.01	1.13± 0.01	0.97± 0.04	88.54	y = -0.0034x + 3.2688
Alkaline Water (pH 9.2)	T_1	1.01 0.04	0.92± 0.01	0.80± 0.05	0.64± 0.01	0.54± 0.01	0.45± 0.01	79.22	y = -0.0038x + 2.9704
	T_2	1.85± 0.15	1.75± 0.03	1.62± 0.02	1.36± 0.24	1.11± 0.01	0.96± 0.02	94.07	y = -0.0032x + 3.2539

T_1 =1ppm , T_2 =2ppm

Table 5: Dissipation of imidacloprid in different soil

Soil	Dose	Concentration remaining in soil (µg/g) (±S.D) on day						$T_{1/2}$ (Days)	Regression equation
		0	5	15	30	60	90		
Jhargram	T_1	0.95±0.06	0.88±0.05	0.77±0.03	0.69±0.06	0.48±0.01	0.32±0.01	59.03	y = -0.0051x+2.9760
	T_2	1.95±0.09	1.83±0.04	1.68±0.04	1.37±0.08	0.97±0.09	0.68±0.05	59.03	y = -0.0051x+3.2923
Mohanpur	T_1	0.96±0.06	0.87±0.04	0.80±0.05	0.71±0.04	0.53±0.07	0.39±0.03	66.9	y = -0.0045x+2.9682
	T_2	2.17±0.15	1.86±0.11	1.59±0.03	1.34±0.02	1.03±0.01	0.90±0.02	70.01	y = -0.0043x+3.2719
Canning	T_1	1.05±0.05	0.84±0.04	0.81±0.02	0.64±0.03	0.48±0.03	0.37±0.02	64.05	y = -0.0047x+2.9757
	T_2	2.05±0.13	1.65±0.03	1.57±0.01	1.31±0.09	1.09±0.03	0.80±0.04	75.26	y = -0.004x+3.2654
Pune	T_1	1.02±0.05	0.95±0.02	0.75±0.06	0.69±0.07	0.58±0.04	0.37±0.02	66.9	y = -0.0045x+2.9875
	T_2	2.05±0.18	1.78±0.09	1.75±0.01	1.44±0.04	1.11±0.08	0.83±0.08	71.67	y = -0.0042x+3.2940

T_1 =1ppm , T_2 =2ppm

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