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Persistence study of Imidacloprid in different soils under laboratory conditions

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ABSTRACT

Background

Chemical pesticides are the most important component of any pest management strategy. Soil an important component of the environment, act as a sink for the pesticides used in agriculture. Persistence of imidacloprid was studied under laboratory conditions in four types of soil viz.sandy loam, clay, red and black soils following treatment at 1.0, 2.0 and 4.0µg/g fortification levels. The imidacloprid residue in the soil samples were measured by validated analytical method.

Results

The dissipation of imidacloprid was found to be faster in black soil followed by sandy loam, clay and red soil with half life value of 50.10, 42.74 and 45.69, respectively. The half life value was varied from concentration of imidacloprid in soil. The faster dissipation in black soil could be attributed to higher pH (7.47) and high organic matter (0.86%) as compared to other soil.

Conclusion

The degradation of imidacloprid in soil depends upon organic carbon content, moisture and soil pH. In general the imidacloprid were found safe from environmental contamination point of view as their half-life value were less than 50 days in all other soils.

Keywords: HPLC; Imidacloprid; Residues; Soil.

1. Introduction

Imidacloprid is a chloronicotinylnitroguanidine insecticide, the IUPAC name is 1-[(6-chloropyridin-3-yl)–n-nitro-4,5-dihydroimidazol-2-amine. The pesticides present in soil sometimes act as a source of contamination for succeeding crop. From soil, the pesticides residues can reach water bodies by leaching and runoff. Pesticides are inherently toxic molecules. Once they reach the water bodies, they start adversely affecting the aquatic environment. Presence of pesticides residue in ground water is extremely hazardous to human beings as ground water is major source of drinking water. Imidacloprid is outstanding biological efficacy, a broad spectrum of activities, low toxicity to warm blooded animals and

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good plant compatibility. Because of its excellent systemic properties imidacloprid is used as a seed dressing as well as for foliar, soil and stem treatment (Ishaaya *et.al.* 1998). The imidacloprid degradation rate, solubility and relative immobility was reported (Krohn-J *et.al.* 2002) under field conditions. The present investigation was, therefore undertaken to evaluate the effect of different soil conditions on the dissipation of imidacloprid in soil. The pesticides concentration and soil characteristics such as pH, temperature, moisture and cation exchange capacity are very important for degradation of imidacloprid in soil under laboratory condition. To objective of study to evaluate the residue level and half life of imidacloprid.

2. Materials and method

2.1 Soil characterization

The soil characterization was performed to determine different physico-chemical properties viz., pH, organic carbon, water holding capacity (WHC) and clay content (particle size distribution) of soils collected from different parts of Gujarat India. The soil sampling based on general sampling procedures and brought back to the laboratory in polyethylene bags. The soils were grounded in order to break the clods without any damage to the physical, chemical and biological characteristics. The soils were air dried and sieved through a 2 mm sieve. The methods followed were as per [4, 5] Walkley, A. and Black, I. A. (1934) and Baruah, T. C. and Barthakur, H. P. (1997).

The test soils were collected from different parts of in Gujarat viz, (a) Vadu, Gujarat (b) Bardoli, Gujarat; (c) Umarsadi, Gujarat (d) Vikram Farm, valvada and were coded as Soil-1 (sandy loam soil), Soil- 2 (clay soil), Soil-3 (red soil), and Soil-4 (black soil), respectively. Based on organic carbon (%), pH and clay content, the soils i.e. Soil-1, Soil- 2, Soil-3, and Soil-4, were classified (soil classification, [6]*OECD N° 106). The soil characteristics data is depicted Table 1. These soils were used for residue and persistence study of imidacloprid under laboratory condition at 25 ± 2 °C.

2.2 Experiment setup under laboratory condition

The experiment was carried out under laboratory condition for residues and persistence study of imidacloprid in soil at 25 ± 2 °C. A quantity of 50g each soil i.e. sandy loam, clay, red and black soil was weighted and transferred into a beaker of 100 mL capacity and fortify at three levels 1, 2 and 4 ug/g with three replication by adding with reference standard of imidacloprid, separately. During entire study period, the soil moisture was maintained at one third of water holding capacity by adding distilled water in regular intervals. The beaker was covered with polythene sheets with few holes and store at 25 ± 2 °C. The periodic sample was drawn at intervals of 0, 1, 3, 15, 30, 45, 60, and 90 days after application. The samples were drawn three replication of each treatment and along with control.

2.3 Extraction and sample clean-up

A 50g representative soil sample was weighted and transferred into 250 mL capacity of Erlenmeyer flask and volume of 100 ml methanol was added into same flask. The Erlenmeyer flask was placed onto orbital shaker for 30 minutes. After shaking, the solutions were filtered into the round bottom flask of 500 mL capacity through Whatman filter paper No.1 by passing a bed of anhydrous sodium sulphate. The residual cake was re-extracted twice with additional volume of 50 mL methanol. The methanol extract were collected, pooled and concentrated to near dryness 5 to 10 mL using vacuum evaporator at ≤ 40 °C. The concentrated extract was subjected to further clean up by column chromatography.

2.3.1 Clean-up by column chromatography

The chromatographic, column [60 cm x 25 mm (OD) was packed with 10g activated florisil with 2-3 cm layer of anhydrous sodium sulphate. The column was pre- conditioned with 25 mL of methanol and concentrated extract were loaded onto the top of the column and eluted with 100ml acetonitrile. Eluate was concentrated to dryness using rotary vacuum evaporator at ≤ 40 °C and residue re-dissolved in 5mL acetonitrile. The samples were transferred into volumetric flask 10 mL capacity using Whatman No. 1 filter paper and final volume was made unto the mark with acetonitrile. The quantitative determination of imidacloprid residues in soil was using reversed phase HPLC with following parameters.

3. Instrumental parameters

Instrument	: Shimadzu LC-2010 AHT with LC-solution software
Column	: C-18 column [Phenomenex, 25cm length x 4.6 mm i.d. and 0.5mu particle size],
Mobile phase	: 0.01% acetic acid in water and acetonitrile (60:40v/v).
Wavelength	: 252 nm
Flow rate	: 1.0 mL
Injection volume	: 20 µl
Retention Time	: 4.93minute

4. Result and discussion

4.1 Method validation

The HPLC method has been validated for determination of low level of imidacloprid in/on different soils viz. sandy loam, clay, red and black soil (Prakash S. *et. al.* 2011). The linearity of the detector response was tested for imidacloprid, in solvent and in matrix over the range of 0.02 to 5.00 µg/mL. A very precise linear relation between the injected amount and the resulting peak area was observed over the entire range with correlation coefficients (r) 0.999. The accuracy and precision of the method was evaluated on the basis of the recoveries obtained for fortified soil samples. The limit of detection (LOD) was 0.006 µg/g and limit of quantitation (LOQ) was 0.02 µg/g for imidacloprid in soil. Recoveries for imidacloprid were 95.18, 94.66, 95.27 and 94.78 % in black, red, sandy loam and clay soil, respectively.The resulting mean recovery ranged varied from 94.66 to 95.27% in soil with relative standard deviations (%RSD) between 1.21 to 3.37% in sandy loam, clay, red and black soil. These data were demonstrated, the excellent sensitivity, selectivity and precise method for determination of imidacloprid residues in soils.

The residue and persistence data of imidacloprid in four type's soil are depicted in table 2. The initial deposits of imidacloprid varied from 0.81 – 0.87 µg g^{-1} in sandy loam soil, clay soil, black and red soil @ 1.0mg/kg. The initial deposits of imidacloprid varied from 1.69 – 1.74 µg g^{-1} and 3.39-3.45 µg g^{-1} in sandy loam soil, clay soil, black and red soil @ 2.0 and 4.0µg/g. The % dissipation of imidacloprid in/on soil treated @ 1mg/kg was 30.59, 39.29, 39.51 and 39.80% after 15 days of application in sandy loam, clay, black and red soil respectively and the corresponding value @ 2 and 4µg/g was 26.4, 38.95, 37.85, 33.91% and 25.66, 35.88, 35.10 and 32.75% respectively. The dissipation of imidacloprid in different soils followed first order kinetics with half life value varying from 39.10 – 50.10 days table 3. Simillar half life values have been reported earlier for imidacloprid. (Sarkar-MA *et. al*.) dissipation of imidacloprid in soil DT50 values ranged from 28.7 to 47.8 days. The shortest half-lives (28.7 and 35.8 days) were observed in the lateritic soil of Jhargram for both liquid and powder formulations. The residue data was subjected to first order kinetics Log Ct= LogCo-kt/2.303, where Ct is concentration after a lapse of time't', Co is apparent initial concentration and 'K' is the dissipation constant. The data ie log residue and time was subjected to simple linear regression analysis (Y=a-bx) and the volue of K was calculated by the formula: k= bx2.303. The value of half life was calculated from the volue of k by the formula: $t_{1/2}$= 0.693/k. The dissipation of imidacloprid was found to be faster in black soil followed by sandy loam, clay and red soil with half life value of 50.10, 42.74 and 45.69, respectively. The half life value was varied from concentration of imidacloprid in soil. The faster dissipation in balck soil could be attributed to higher pH (7.47) and high organic matter (0.86%) as compared to other soils, which might have induced greater microbial activity. Similler results have also been reported (Suparna pal *et. al*). The dissipation was faster under alkaline condition followed by acidic and neutral. The bioefficacy of pyrazosulfuron-ethyl may be affected as it suffers faster degradation in alkaline soil. We also found that black soil higher pH than other soil. The degradation of imidacloprid in black soil faster than other soil.

5. Conclusion

The effect of soil characteristics and dose on the dissipation of imidacloprid from different type of soil. The degradation of imidacloprid in soil depends upon organic carbon content, moisture and soil pH. In general the imidacloprid were found safe from environmental contamination point of view as their half-life value were less than 50 days in all other soils.

Table 1: Characteristics of soil

Soil Sampling (Location)	Characteristics								Soil Type
	Organic Carbon (%)	pH (0.01 M $CaCl_2$)	pH Distilled Water	Particle Size					
				Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Water Holding Capacity	
Valvada	0.86	7.15	7.47	3.64	10.64	19.01	38.00	60.06	Black soil
Bardoli	1.37	6.60	6.91	2.42	9.18	10.73	53.68	67.06	Clay Soil
Umarsadi	0.42	4.32	4.82	10.13	7.47	7.98	42.55	65.74	Red Soil
Baroda	0.84	7.00	7.25	1.67	59.96	5.06	15.20	47.51	Sandy loam Soil

Table 2: Residue and degradation of Imidacloprid in different soils

DAT	Persistence of Imidacloprid in Different Soils											
	Sandy loam soil			Clay soil			Red soil			Black oil		
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}
0	0.85	1.70	3.39	0.84	1.72	3.40	0.81	1.69	3.39	0.87	1.74	3.45
1	0.81 (4.71)	1.64 (3.53)	3.29 (2..95)	0.77 (8.33)	1.60 (6.98)	3.20 (5.88)	0.78 (3.70)	1.63 (3.55)	3.27 (3.54)	0.82 (5.75)	1.65 (5.17)	3.28 (4.93)
3	0.75 (11.76)	1.53 (10.00)	3.10 (8.55)	0.64 (23.81)	1.35 (21.51)	2.68 (21.18)	0.65 (19.75)	1.40 17.16	2.88 (15.04)	0.74 (14.94)	1.51 (13.22)	3.02 (12.46)
7	0.68 (20.00)	1.40 (17.65)	2.82 (16.81)	0.59 (29.76)	1.21 (29.65)	2.45 (27.94)	0.58 (28.40)	1.27 (24.85)	2.65 (21.83)	0.65 (25.29)	1.32 (24.14)	2.72 (21.16)
15	0.59 (30.59)	1.25 (26.47)	2.52 (25.66)	0.51 (39.29)	1.05 (38.95)	2.18 (35.88)	0.49 (39.51)	1.05 (37.85)	2.20 (35.10)	0.53 (39.08)	1.15 (33.91)	2.32 (32.75)
30	0.52 (38.82)	1.15 (32.35)	2.31 (31.86)	0.45 (46.43)	0.95 (44.77)	1.89 (44.41)	0.39 (51.85)	0.84 (50.30)	1.70 (49.85)	0.41 (52.87)	0.85 (51.15)	1.81 (47.54)
45	0.48 (43.53)	0.98 (42.35)	2.06 (39.23)	0.33 (60.71)	0.68 (60.47)	1.35 (60.29)	0.32 (60.49)	0.67 (60.36)	1.35 (60.18)	0.31 (64.37)	0.68 (60.92)	1.35 (60.87)
60	0.32 (62.35)	0.65 (61.76)	1.35 (60.18)	0.25 (70.24)	0.52 (69.77)	1.16 (65.88)	0.22 (72.84)	0.50 (70.41)	1.14 (66.37)	0.25 (71.26)	0.51 (70.69)	1.15 (66.67)
90	0.19 (77.65)	0.51 (70.00)	1.05 (69.03)	0.15 (82.14)	0.35 (79.65)	0.72 (78.82)	0.19 (76.54)	0.42 (75.15)	0.86 (74.63)	0.15 (82.76)	0.32 (81.71)	0.82 (79.13)

DAT= Days after application
Figure in parentheses are present degradation

Table 3: Effect of soil characteristics and dose on the dissipation of Imidacloprid in soil

Soil types	Half life –Value			Mean
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	
Sandy loam soil	44.47	53.45	55.07	50.10
Clay soil	40.89	42.89	44.44	42.74
Red soil	44.77	45.60	46.70	45.69
Black oil	37.46	38.37	41.46	39.10
Mean	41.90	45.08	46..92	44.63

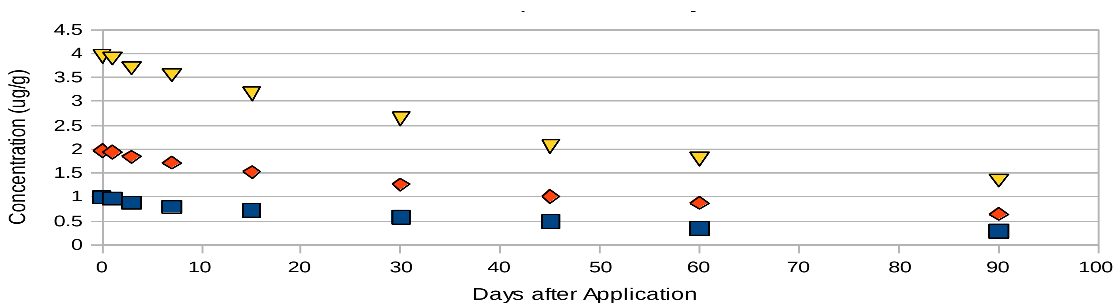

Figure 1: Residue of Imidacloprid in Sandy Loam soil

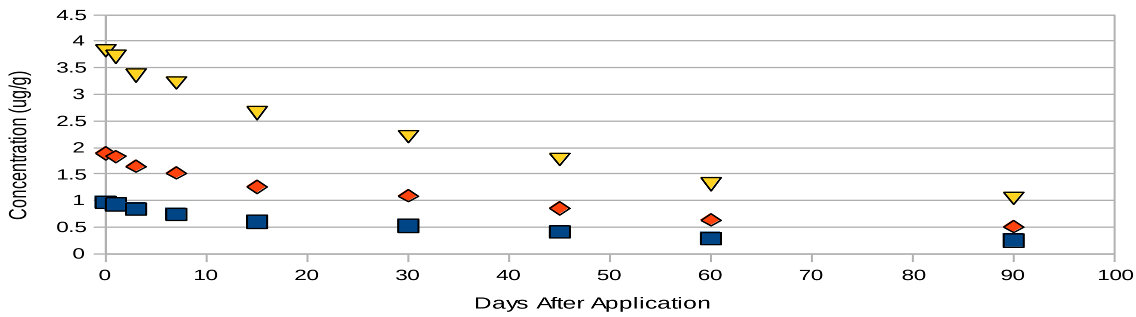

Figure 2: Residue of Imidacloprid in Clay soil

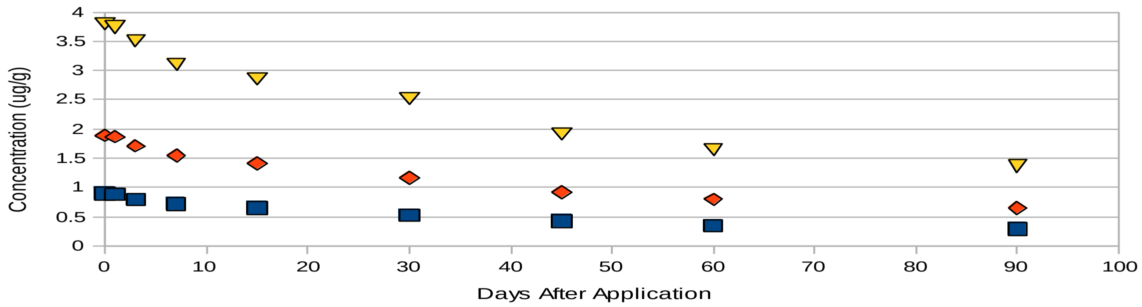

Figure 3: Residue of Imidacloprid in Red soil

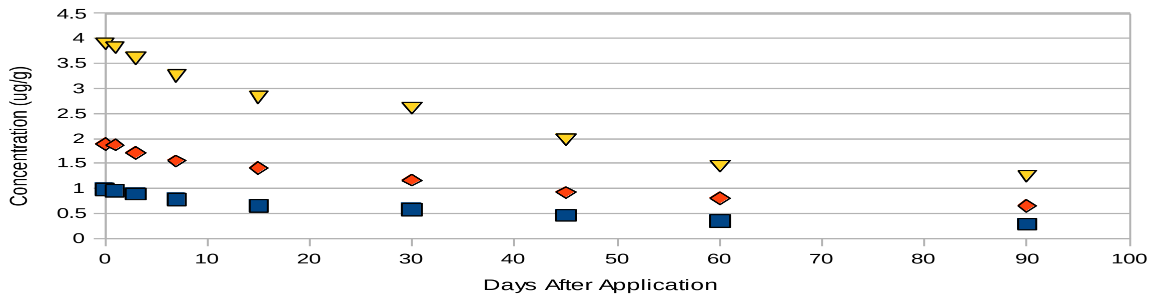

Figure 4: Residue of Imidacloprid in Black soil

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