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Persistence of Acetamiprid in Soil

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Crops, which are the main source of food for humans, are attacked by various disease causing organisms like viruses, fungi, insects, nematodes, etc. Weeds are another threat to agriculturally grown crops. It is estimated that one third of the world's food crop is destroyed by these pests annually. Chemical pesticides play an important role in increasing crop production by reducing the incidence of pest attacks. Pesticides are inherently poisonous molecules and have the potential to cause harm to the environment if not used properly. However, their use in agriculture is inevitable, especially in developing countries to sustain the growing population. When a pesticide is applied in the field a major amount falls on to the soil surface. Once present in the soil, the pesticide finds its way into various other compartments of the environment and acts as source of contamination to air and groundwater. The contamination potential of any pesticide depends on its residential period in soil. Therefore, it is necessary to study the persistence behavior of pesticides in soil.

Acetamiprid ((E)-N-[(6– chloro-3- pyridyl) methyl]-N'-cyano-N- methyl-acetamidine) (Fig. 1) is an insecticide belonging to the neonicotinoid group. It shows excellent efficacy against aphids, leafhoppers, whiteflies, thrips, leaf beetles, leafminer moth, termites, etc. in various crops like okra (Sonalkar, 1997; Acharya et al., 2002; Singh and Kulshrestha, 2005), gram (Gupta et al., 2005), mustard (Pramanik et al., 2006), strawberry (Labanowska, 2002), cotton (Singh et al., 2002), and citrus (Li et al., 2000). Acetamiprid has a unique mode of action, which enables it to control insects that have developed resistance to organphosphorus insecticides. A review of the literature has revealed that no work has been carried out on the fate of acetamiprid in soil. Therefore, studies were undertaken to determine the persistence behavior of acetamiprid in alluvial soil of Delhi under laboratory conditions.

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Materials and Methods

Analytical grade acetamiprid (purity 99.6%) was obtained from De-Nocil, India. Standard stock solution (1000 μg/ml) was prepared in a high-performance liquid chromatography (HPLC) grade acetonitrile. Lower dilutions were prepared by taking required aliquot from the stock solution and diluting it with HPLC grade acetonitrile.

Organic solvents like acetone and dichloromethane were glass distilled. An aqueous solution of NaCl (10%) was partitioned twice with dichloromethane to remove the impurities. Sodium sulfate was washed with acetone, dried at room temperature, and then activated at 110°C for four hours before use.

Fresh surface soil (0–15 cm in depth) was collected from the fields of the Indian Agricultural Research Institute, New Delhi, India. The soil was air-dried under shade, ground, sieved through a 2 mm mesh screen, and stored in plastic container until used. The physico-chemical properties of the soil (type: inceptisol) were: pH 7.69, organic carbon 0.501%, clay 5%, sand 77.5%, silt 17.5%, texture sandy loam, and field capacity moisture content 20%.

The persistence of acetamiprid in alluvial soil was studied at two concentration levels, 1 and 10 μg/g, and under three moisture regimes, dry, field capacity, and submerged in incubator chamber at 25°C. For fortification

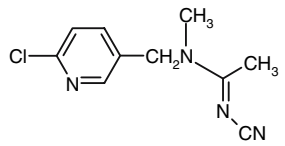

Fig. 1 Structure and properties of acetamiprid

of the soil at 100 µg/g level, 100 g soil was taken in a beaker and 10 ml of standard solution of acetamiprid (1,000 µg/ml, in acetonitrile) was added. Additional acetone was added to dip the soil completely. Soil was stirred with a glass rod for uniform mixing and the contents were left undisturbed overnight for the evaporation of the solvent. After the complete evaporation of the solvent, the fortified soil was again mixed and then serially diluted with untreated soil to get a 10.0 and 1.0 µg/g level of fortification. For 10 µg/g treatment, 900 g untreated soil was taken in a polythene bag and 100 g of fortified soil (100 µg/g) was added and thoroughly mixed for homogeneity. For the 1.0 µg/g treatment, 10 µg/g treated soil was mixed with untreated soil in the ratio 1:9. The homogeneity of the treated soil was checked by drawing three samples from each treatment, and analyzing them for residues. As there was not much variation in the residues among replicates, the treated soil was assumed as homogeneous. Treated soil samples (20 g air-dry weight) were transferred to beakers. Untreated control soil samples were also maintained simultaneously for each experiment. For treatment under the field capacity moisture regime, a calculated amount of water was added to bring the soil to field capacity moisture level. In the case of submerged condition, enough water was added to raise the level of water to about 3 cm above the soil level. In the dry treatment no water was added in the beakers. All the beakers of field capacity and submerged treatments were weighed, and constant weights of the beakers were maintained throughout the experiment by adding the lost water daily. The beakers were placed in a thermostatically controlled incubator at 25±1°C and > 90% relative humidity. Three beakers from each treatment were drawn along with the control at different time intervals and analyzed for acetamiprid residues.

The soil samples were extracted with acetone. The soil samples were suspended in acetone (~50 ml), shaken for 30 minutes, and the contents were filtered. The extraction procedure was repeated two more times. The combined extract was concentrated in a rotary evaporator. The remaining aqueous phase was transferred into the separatory funnel, diluted with 10% NaCl solution (~150 ml), and extracted with dichloromethane (3 x 30 ml). The combined organic phase was passed through anhydrous Na_2SO_4.

Extracts obtained from different experiments were concentrated to dryness in a rotary evaporator. The residues were dissolved in 5 ml acetonitrile. The determination of acetamiprid was carried out by HPLC using Water's instrument equipped with the column RP C-18 (250 mm x 4 mm, 10 µm), the detector variable UV-visible (model 484), a binary pump (model 501) and an injector rheodyne (20 µl loop). The operating parameters were: λ_{max} 254 nm, injection volume 20 µl, solvent system acetonitrile-water gradient as given in Table 1.

Table 1 Gradient conditions

Time	Flow (ml/min)	% Acetonitrile	% Water
0	1.0	10	90
6	1.0	15	85
12	1.0	30	70
15	1.0	100	0
17	1.0	100	0
20	1.0	10	90
25	1.0	10	90

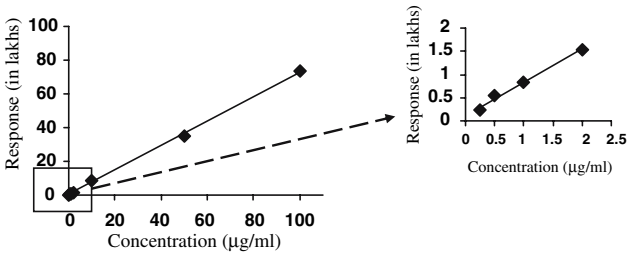

Fig. 2 Linearity curve of acetamiprid

Under these conditions the retention time of acetamiprid was 10.5 minutes. The minimum detection limit for pure compound was 5 ng with linearity range 5–2,000 ng (Fig. 2). The limit of quantification was found to be 0.005 µg/g for soil samples.

The efficiency of the method was evaluated by carrying out a recovery experiment. The untreated soil samples (20 g air dry), in triplicate, were fortified at 0.1 and 1 µg/g levels. They were processed and analyzed by HPLC as described above.

Persistence data was fitted into first-order dissipation kinetics

$$C = C_o e^{-Kt}$$

Where C = concentration after a lapse of time t, C_o = apparent initial concentration and K = rate constant.

In all cases, the first order equation provided a satisfactory fit for the data ($r > 0.9$) and the half-life values were calculated based on this.

Results and Discussion

The recoveries of acetamiprid from soil samples fortified at 0.1 and 1.0 µg/g level varied from 81–93%. Since recoveries were more than 80%, the residue data has not been corrected for the recoveries.

Persistence of acetamiprid in soil under laboratory conditions in a thermostatically controlled incubating chamber was studied at two levels of application 1.0 and 10.0 µg/g, and under three moisture regimes: air-dry, field capacity moisture, and submerged. The residue data for different treatments are presented in Table 2.

Following the treatment of soil at 1.0 and 10.0 µg/g level, the average initial deposits varied from 0.83–0.84 and 8.43–8.62 µg/g. The residues persisted beyond 60 days in all the treatments and 10.4–62.1% loss was recorded on day 7, 29.8–88.0% on day 30, and 35.5–95.7% on day 60 (Fig. 3). The dissipation of residues in different treatments followed first-order kinetics, with correlation coefficient ranging from 0.81 to 0.98. The calculated half-life values ranged from 15.7–150.5 days under different treatments (Table 2).

Under field capacity moisture conditions more than 90% dissipation was recorded on the 60th day at both the fortification levels. Dissipation was somewhat slower at low level ($T_{1/2}$ 17.4 days) than at high level ($T_{1/2}$ 15.7 days) of fortification. Under submerged condition, the 60th day sampling recorded the loss of 80–92% of the applied acetamiprid. It dissipated faster at the 1 µg/g level ($T_{1/2}$ 19.2 days) than at the 10 µg/g level ($T_{1/2}$ 29.8 days). Under the dry condition dissipation was very slow and less than 40% dissipation was recorded on the 60th day at both levels.

Among the field capacity and submerged moisture regimes acetamiprid persisted longer under the submerged

Table 2 Persistence of acetamiprid in soil

Days after application	Average residues in µg/g ± SD					
	Dry		Field capacity		Submerged	
	1.0	10.0	1.0	10.0	1.0	10.0
0	0.83 ± 0.15	8.43 ± 0.51	0.86 ± 0.05	8.62 ± 0.09	0.84 ± 0.10	8.43 ± 0.36
3	0.77 ± 0.02	7.83 ± 0.99	0.62 ± 0.04	4.30 ± 0.28	0.58 ± 0.10	6.06 ± 0.23
5	-	-	0.55 ± 0.02	3.27 ± 0.11	0.58 ± 0.07	5.91 ± 0.13
7	0.73 ± 0.01	7.56 ± 0.81	0.50 ± 0.01	2.75 ± 0.28	0.53 ± 0.01	5.79 ± 0.15
10	0.64 ± 0.02	6.96 ± 0.13	0.42 ± 0.03	2.05 ± 0.08	0.44 ± 0.06	4.98 ± 0.21
15	0.59 ± 0.05	6.16 ± 0.42	0.31 ± 0.03	1.61 ± 0.23	0.36 ± 0.03	3.53 ± 0.16
30	0.58 ± 0.05	5.68 ± 0.17	0.23 ± 0.05	1.03 ± 0.04	0.27 ± 0.05	2.74 ± 0.36
45	0.55 ± 0.06	5.37 ± 0.16	0.11 ± 0.06	0.63 ± 0.09	0.18 ± 0.01	2.06 ± 0.08
60	0.54 ± 0.04	5.17 ± 0.07	0.07 ± 0.01	0.37 ± 0.03	0.07 ± 0.01	1.64 ± 0.26
90	0.52 ± 0.01	5.11 ± 0.14	-	-	-	0.88 ± 0.13
Half-life $T_{1/2}$ (days)	150.5	125.4	17.4	15.7	19.2	29.8

- = Sample not drawn

SD = Standard deviation

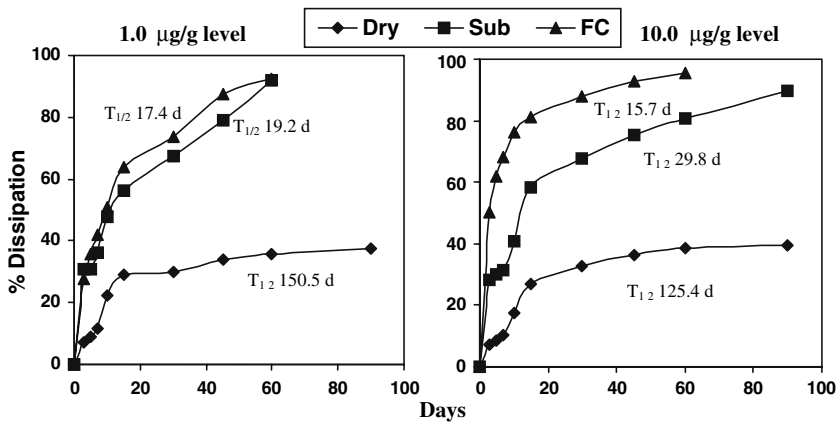

Fig. 3 Dissipation of acetamiprid in soil

condition. The half-life values varied from 15.7–17.4 days under field capacity and 19.2–29.8 days under the submerged condition. It seems aerobic microbes are more efficient in degrading acetamiprid than anaerobic microbes. Faster degradation under field capacity moisture has also been reported for temephos (Prasad and Jain, 1990) and chlorpyriphos (Awasthi and Prakash, 1997).

The longer persistence, and hence slower dissipation, under air-dry conditions could be attributed to the low microbial activity in dry soil. Miles et al. (1984) have also attributed the slower dissipation of chlorfenvinphos in dry soil as compared to moist soil, to lower microbial activity. Similar results have also been reported for 2,4-D (Johnson et al., 1995), imazaquin (Baughman and Shaw, 1996), chlorothalonil (Choudhury and Awasthi, 2000) and β-cyfluthrin (Gupta and Gajbhiye, 2002). However, such dry conditions are not likely to occur in fields under cropped conditions.

As is evident, the level of fortification had no effect on the rate of dissipation of acetamiprid in soil maintained at the field capacity moisture level. However, under submerged conditions, the rate of dissipation was faster at a low level than at a high level of fortification, which could probably be attributed to the inhibition of anaerobic microbes at a higher level of application. The reverse trend was observed under the dry soil condition where dissipation was somewhat faster at a higher level than low. Similar trend in dissipation in air-dry soil has been reported for thifluzamide (Gupta and Gajbhiye, 2004).

The study clearly shows that acetamiprid has moderate persistence in soil under field capacity and submerged moisture regimes, under laboratory conditions. Besides, under natural field conditions, the persistence is likely to be less due to harsh conditions of temperature, exposure to sunlight, etc. Thus, use of acetamiprid in crop protection is unlikely to pose residual problem.

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