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Effect of Light on the Degradation of Two Neonicotinoids viz Acetamiprid and Thiacloprid in Soil

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Abstract Persistence of two neonicotinoids viz thiacloprid and acetamiprid in soil as affected by UV and sunlight exposure was studied. Treated soil was placed in petriplates, brought to field capacity moisture and then exposed to UV and sunlight. Dissipation for both the pesticides followed monophasic first order kinetics under sunlight, however under UV-light biphasic dissipation was recorded. Residues of acetamiprid and thiacloprid in soil dissipated with half-lives of 11.1 and 12.8 days under UV light and 25.1 and 19.1 days under sunlight, respectively. Residues of both the neonicotinoids dissipated quickly under UV light as compared to sunlight. Exposure of thin film of acetamiprid and thiacloprid to UV and sunlight revealed that acetamiprid is more photo labile than thiacloprid. More than 95% acetamiprid dissipated within 24 h as compared to ~70% dissipation observed for thiacloprid.

Keywords Thiacloprid · Acetamiprid · Dissipation · Soil · Ultra violet light · Sunlight

Pesticides, used in agriculture or in public health control, reach the soil either by direct application or by spray drift. Once in the soil, pesticides undergo various dissipation processes like microbial degradation, chemical hydrolysis, photolysis, volatilization, leaching and surface runoff. The contribution made by each of these dissipation processes towards the overall dissipation depends upon the nature of soil, pesticides and other environmental factor. It has been reported in literature that among various biotic and abiotic transformation processes, photodegradation is an important factor influencing the fate of pesticides in the field (Konstantinou et al. 2001). In practice also it has been observed that pesticides persist longer under laboratory studies as compared to field studies (Sanyal et al. 2000; Ganier et al. 1996; Fernandez et al. 2001). Also surface residues following foliar spray degrade faster than the translocated residues inside plant matrix even though physiological activity is more inside the plant matrix. Faster degradation of highly persistent DDT under sunlight as compared to samples kept under dark has already been reported (Miller and Zepp 1983). All these observations emphasise on the important role played by light in pesticide degradation.

Thiacloprid (*N*-(3-(6-chloro-pyridin-3-ylmethyl)-thiazolidin-2-ylidene)-cyanamide) and acetamiprid ((E)-*N*-[(6-chloro-3-pyridyl) methyl]-*N*′-cyano-*N*-methyl-acetamidine) (Fig. 1) belong to neonicotinoid group of insecticides. They have been found effective for the control of sucking insect pests such as aphids, whiteflies, jassids, thrips, leafminer, beetles etc. in various crops like okra, gram, mustard, cotton, citrus, etc. (Albuquerque et al. 1999; Li et al. 2000; Branco and Pontes 2001; Boselli and Vergnani 2001; Singh and Kulshrestha 2005; Gupta et al. 2005; Pramanik et al. 2006). The effect of light on persistence of thiacloprid and acetamiprid has not been reported in literature so far. Therefore, the present experiments were conducted to study the effect of light (sunlight and UV light) on persistence of these two neonicotinoids in soil.

Materials and Methods

Soil required for the study was collected from the plough layer (0–15 cm depth) of the research farm of Indian

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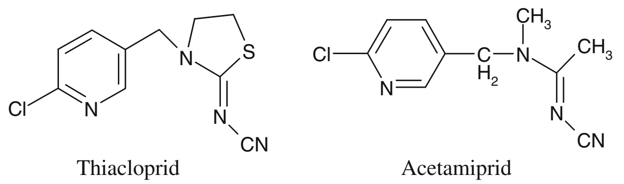

Thiacloprid Acetamiprid

Fig. 1 Chemical structures of thiacloprid and acetamiprid

Agricultural Research Institute, New Delhi, India, with no history of pesticide application. It was air-dried in the shade, ground, sieved through a 2-mm mesh screen. 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%. Analytical grade thiacloprid (purity 99.7%) and acetamiprid (purity 99.6%) were obtained from M/s Bayer India Ltd and De-Nocil, India, respectively. Separate stock solutions of thiacloprid and acetamiprid ($\sim$1,000 µg mL^{-1}) were prepared by dissolving the accurately weighed materials in HPLC grade acetonitrile. Solutions of lower concentrations were obtained by serially diluting the stock solutions with acetonitrile. Organic solvents like hexane, acetone and dichloromethane were glass distilled before use. Sodium sulfate was washed with acetone and then activated at 110°C for 4 h before use. HPLC grade solvents were procured from Merck India Ltd. These were filtered and de-gassed prior to use.

Soil (100 g) was taken in a beaker and required quantity of standard stock solution (1,000 mg L^{-1}) of thiacloprid was added to get 100 mg kg^{-1} concentration. Additional acetone was added to dip the soil, stirred with glass rod for uniform distribution of pesticide and then left undisturbed till complete evaporation of acetone. The dry soil was again mixed. This fortified soil was diluted with untreated soil in the ratio 1:9 to get 10 mg kg^{-1} fortification level. Again the soil was mixed thoroughly. The homogeneity of treated soil was tested by randomly drawing three samples from the treated soil and analyzing them. Since there was not much variation among replicates, the treated soil was considered homogeneous. The treated soil samples (20 g) were transferred and spread uniformly in petri-plates (10 cm i.d.) and soil was brought to the field capacity moisture level by adding 4 mL water in each plate. All the petri-plates were weighed and divided into two sets. One set of petri-plates was exposed to UV light and the second set was kept in open under sunlight. The water lost was replenished daily by weighing the petri-plates. Samples kept under sunlight and UV light were exposed for 6 h daily. Similar set of experiment was conducted with acetamiprid. To study the stability of thiacloprid and acetamiprid to UV and sunlight, another experiment was conducted with thin film of pure compounds on glass surface. Standard solution of thiacloprid (1 mL, 100 mg L^{-1}) was spread on petri-plates (10 cm i.d.). Petri-plates were kept on flat surface and left undisturbed for evaporation of solvent. The plates were divided into two sets. One set of petri-plates was exposed to UV light and the other was kept in open under sunlight. Samples were exposed to sunlight/UV light for 6 h daily. Similar set of experiment was conducted with acetamiprid. Samples in duplicate from each treatment were drawn at different time intervals and processed.

Soil samples collected from different experiments were taken in beaker and enough acetone was added to dip the soil. The samples were stirred with glass rod and kept for 30 min with intermittent shaking. The contents were filtered using Whatman filter paper No.1, soil was transferred back to beaker and re-extracted two more times using fresh 50 mL acetone each time. Acetone extracts were pooled and concentrated using rotary evaporator. The concentrated extract was transferred to separatory funnel, diluted with saline solution (200 mL, 10%) and partitioned thrice using dichloromethane (3 × 30 mL). The dichloromethane phases were combined and passed through anhydrous sodium sulfate. The extract was evaporated to dryness using rotary evaporator and the residues dissolved in HPLC grade acetonitrile. Samples of thin film were directly dissolved in acetonitrile, filtered and analysed by HPLC.

Residues of acetamiprid and thiacloprid were estimated by high-pressure liquid chromatography (HPLC). A Waters HPLC equipped with RP-18 column (250 × 4.6 mm, 5 µm), variable UV-visible detector (model 484), binary pump (model 501) and Rheodyne injector (20-µL loop) was used. Both for acetamiprid and thiacloprid the analysis was carried out at $\lambda_{\max}$ 242 nm using acetonitrile-water gradient solvent system as mobile phase at a flow rate of 1 mL min^{-1} (Table 1).

Under these conditions the retention times of acetamiprid and thiacloprid were 14.9 and 10.9 min, respectively. The minimum detection limit for acetamiprid was 5 ng with linearity range 5–2,000 ng and for thiacloprid was 4 ng with linearity range 4–2,000 ng.

Table 1 HPLC gradient conditions for acetamiprid and thiacloprid

Acetamiprid			Thiacloprid		
Time	% Water	% Acetonitrile	Time	% Water	% Acetonitrile
0	90	10	0	85	15
6	85	15	11	60	40
12	70	30	13	10	90
15	0	100	16	10	90
17	0	100	17	85	15
20	90	10	25	85	15
25	90	10			

The residue data were subjected to regression analysis and the fit of the data to first order kinetics ($Ct = Coe^{-Kt}$) was confirmed by testing the statistical significance of correlation coefficient. The half-life values were calculated from dissipation constant calculated from regression analysis.

Results and Discussion

The efficiency of the method was evaluated by carrying out recovery experiment. The untreated soil samples (20 g air dry), in triplicate, were fortified, processed and analyzed by HPLC as described above. The recoveries of acetamiprid from soil samples fortified at 0.1 and 1.0 $\mu g\ g^{-1}$ level varied from 81–93% and that of thiacloprid fortified at 0.05 and 0.5 $\mu g\ g^{-1}$ level varied from 80–86%. Since recoveries were more than 80%, the residue data has not been corrected for the recoveries.

Persistence data of thiacloprid and acetamiprid is presented in Tables 2 and 3. Results revealed that in different treatments residues of both the neonicotinoids persisted beyond 30 days with the overall dissipation of 59.0–99.8%.

Soil incorporated residues of thiacloprid gave average initial deposits of 8.78 $\mu g\ g^{-1}$ (Table 2). Under UV-light, residues dissipated to ∼50% of the initial values within 2 days. Overall dissipation in 30 days was ∼85%. Under sunlight, 4th day and 30th day samples recorded 42.9% and 71.4% dissipation loss, respectively. In case of acetamiprid, initial deposits of 8.61 $\mu g\ g^{-1}$ were reduced to 50% of the initial value in two days under UV light (Table 2). Overall dissipation in 30 days was 88%. However, under sunlight, 2nd, 10th and 30 day samples recorded the loss to the tune of 19.1%, 44.9% and 59%, respectively.

Thin film of thiacloprid on glass surface gave average initial deposits of 90.85 μg/plate (Table 3). On exposure to UV-light, more than 72% dissipation loss was recorded in one day. Overall dissipation on 30th day was ∼97%. Under sunlight, the dissipation of thiacloprid from thin film was slow and 5th day and 30th day samples revealed only ∼25% and 69% dissipation losses, respectively. Thin film of acetamiprid gave initial deposits of 94.59 μg/plate (Table 3). Under UV-light, more than 90% of the residues dissipated in one day. However under sunlight only ∼25% residues were lost in three days. Residues were reduced to ∼17.9 μg/plate on 10th days amounting to the overall loss of ∼81%.

Table 2 Persistence of thiacloprid and acetamiprid in soil under UV light and sunlight

Days	Residues ($\mu g\ g^{-1}$)			
	Thiacloprid		Acetamiprid	
	UV light	Sunlight	UV light	Sunlight
0	8.78	8.78	8.61	8.61
1	5.25 (40.2)	6.50 (25.9)	5.37 (37.6)	7.49 (13.0)
2	4.44 (49.5)	5.92 (32.6)	4.30 (50.1)	6.97 (19.1)
4	2.60 (70.4)	5.02 (42.9)	3.27 (62.1)	6.77 (21.4)
7	2.29 (73.9)	4.31 (50.9)	2.75 (68.1)	5.49 (36.3)
10	1.80 (79.5)	3.75 (57.3)	2.05 (76.2)	4.74 (44.9)
15	1.51 (82.8)	3.38 (61.5)	1.61 (81.3)	4.73 (45.1)
30	1.31 (85.1)	2.51 (71.4)	1.03 (88.0)	3.54 (59.0)

Figure in paranthesis shows % dissipation

Table 3 Persistence of thiacloprid and acetamiprid as thin film under UV light and sunlight

Days	Average amount recovered (μg)			
	Thiacloprid		Acetamiprid	
	UV light	Sunlight	UV light	Sunlight
0	90.85	90.85	94.59	94.59
1	25.10 (72.4)	85.92 (5.4)	7.81 (91.7)	76.80 (18.8)
3	18.04 (80.1)	73.86 (18.7)	2.96 (96.9)	70.75 (25.2)
5	11.62 (87.2)	68.30 (24.8)	1.71 (98.2)	40.09 (57.6)
7	7.55 (91.7)	56.84 (37.4)	1.05 (98.9)	24.53 (74.1)
10	4.15 (95.4)	46.52 (48.8)	0.51 (99.5)	17.92 (81.1)
15	3.42 (96.2)	39.71 (56.3)	0.36 (99.6)	11.86 (87.5)
30	2.59 (97.1)	28.13 (69.0)	0.17 (99.8)	1.18 (98.8)

Figure in paranthesis shows % dissipation

Residue data was subjected to first order dissipation kinetics and the results are presented in Table 4. It was observed that under sunlight dissipation of residues, both as thin film and in soil, followed monophasic first order kinetics (Fig. 2). The dissipation half-lives varied from 4.9 to 25.1 days for acetamiprid and 17.7–19.1 days for thiacloprid (Table 4). However, under UV-light the dissipation of residue was biphasic with very fast dissipation during initial period followed by slower loss (Fig. 2). Dissipation within each phase followed first order kinetics with the correlation coefficient values ranging from 0.86 to 0.98. For acetamiprid half-life of dissipation varied from 0.4 to 1.9 days during initial fast period (0–2 days) and 8.3 to 16.0 days during the slower second phase (4–30 days). The half-life values calculated from forced single phase first order rate dissipation kinetics varied from 4.4 to 11.1 days (Fig. 3).

Similarly, for thiacloprid the residues dissipated with the half-life of 2.7 to 4.8 days during initial period (0–10 days) and 30.4 to 47.8 days during the later period (10–30 days) (Table 4). The half-life values calculated from the forced single phase first order rate dissipation kinetics varied from 7.2 to 12.8 days (Fig. 3). Thus, under UV-light, both for acetamiprid and thiacloprid, single phase first order kinetics underestimates the rate of dissipation during initial

Table 4 Regression equation and half-life for first order dissipation of thiacloprid and acetamiprid

Treatment	Dissipation type	Days	Regression equation	CorreCoeff	$T_{1/2}$ (days)
Thiacloprid					
UV-light, thin film	Single phasic	0–30	Y = −0.0419X + 1.3878	0.66	7.2
	Biphasic	0–10	Y = −0.1113X + 1.6598	0.86	2.7
		10–30	Y = −0.0099X + 0.7079	0.98	30.4
UV-light, soil	Single phasic	0–30	Y = −0.0235X + 1.9584	0.66	12.8
	Biphasic	0–10	Y = −0.0624X + 2.1075	0.86	4.8
		10–30	Y = −0.0063X + 1.6006	0.89	47.8
Sunlight, thin film	Single phasic	0–30	Y = −0.017X + 1.9089	0.93	17.7
Sunlight, soil	Single phasic	0–30	Y = −0.0158X + 0.8066	0.83	19.1
Acetamiprid					
UV-light, thin film	Single phasic	0–30	Y = −0.0683X + 0.8498	0.61	4.4
	Biphasic	0–2	Y = −0.7522X + 1.8656	0.94	0.4
		4–30	Y = −0.0361X + 0.2248	0.88	8.3
UV-light, soil	Single phasic	0–30	Y = −0.027X + 0.7058	0.83	11.1
	Biphasic	0–2	Y = −0.1511X + 0.9173	0.96	1.9
		4–30	Y = −0.0188X + 0.5448	0.94	16
Sunlight, thin film	Single phasic	0–30	Y = −0.0618 + 1.921	0.99	4.9
Sunlight, soil	Single phasic	0–30	Y = −0.012X + 0.869	0.88	25.1

Corre. Coeff.—Correlation Coeffiient

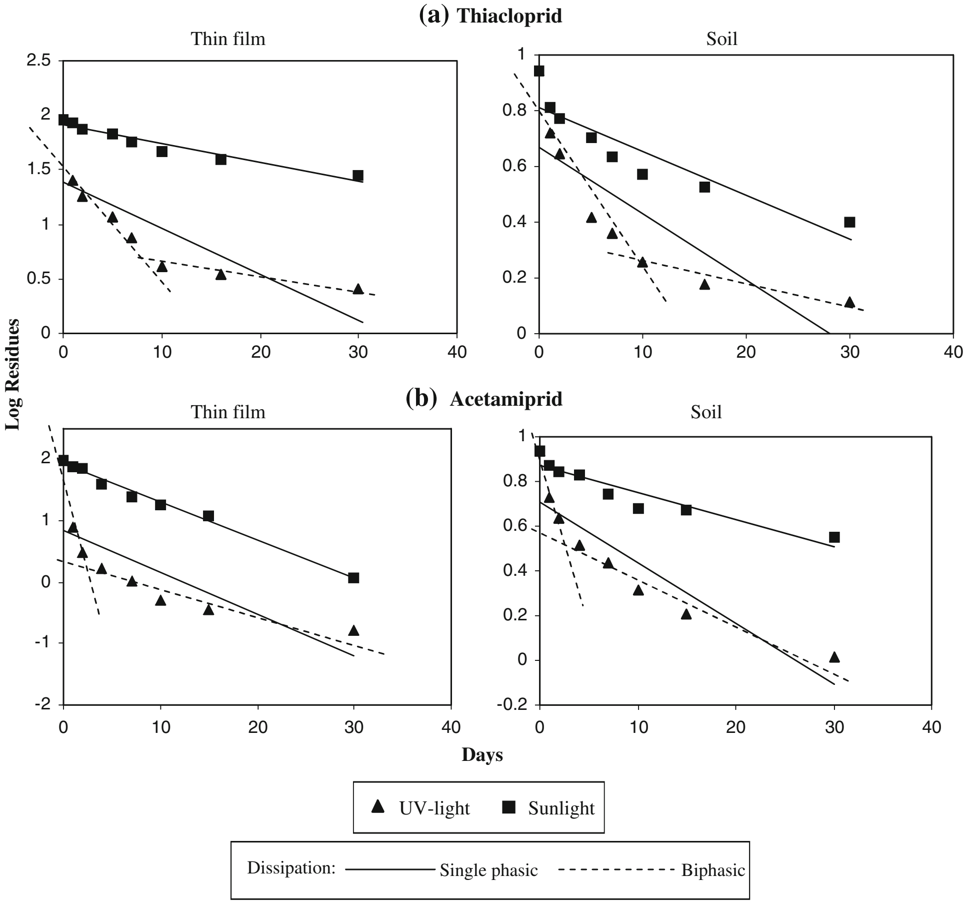

Fig. 2 Dissipation kinetics of (**a**) thiacloprid and (**b**) acetamiprid under UV and sunlight

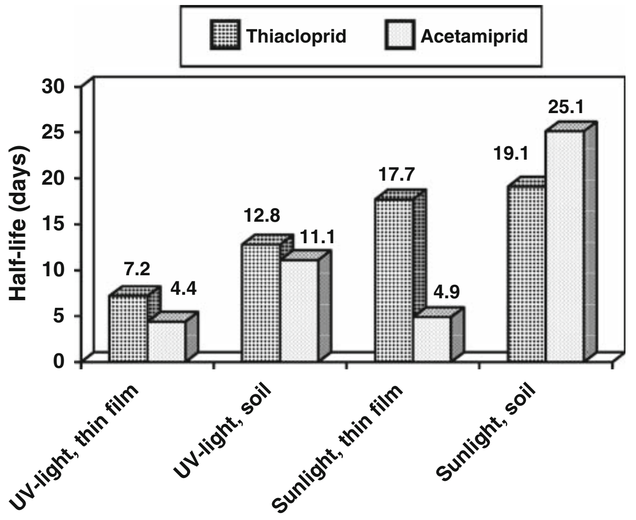

Fig. 3 Half-lives of thiacloprid and acetamiprid based on first order monophasic dissipation kinetics

period and overestimate it during later period. Biphasic dissipation has earlier been reported for acetachlor (Ma et al. 2004) and endosulfan (Whitemyre et al. 2004).

Results showed that both thin film and soil-incorporated residues of the neonicotinoids degrade faster under UV-light ($T_{1/2}$: 4.4–12.8 days) than under sunlight ($T_{1/2}$: 4.9–25.1 days). Faster dissipation under UV-light indicates that UV component of light is a major contributing factor towards the dissipation of these two neonicotinoids. Faster degradation under UV light has earlier been reported for another neonicotinoid thiamethoxam (Gupta et al. 2006).

Results revealed that under both the light regimes viz. UV- and sunlight, residues of soil incorporated neonicotinoids persist longer with the half-life varying from 11.1 to 25.1 days as compared to thin film residues which dissipate with the half-life values ranging from 4.4 to 17.7 days. Longer persistence in soil could be due to the adsorption of pesticides on soil surface. Katagi (2004) has also reported that photodegradation of pesticides on soil surface is influenced by adsorption to clay minerals or solubilization to humic substances. Longer persistence in soil has earlier been reported for another neonicotinoid compound thiamethoxam (Gupta et al. 2006). It is also observed that under different treatments acetamiprid dissipated with the mean half-life of 11.4 days as compared to 14.2 days observed for thiacloprid. Faster dissipation of acetamiprid revealed that it is more photolabile than thiacloprid.

In conclusion, dissipation studies on acetamiprid and thiacloprid under sunlight and UV-light revealed that both the compounds are unstable to light, especially the UV-light. Effect of light on dissipation is more pronounced in case of acetamiprid. Also, presence of soil matrix slows down the dissipation process.

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