Studies on dissipation of thiamethoxam insecticide in two different soils and its residue in potato crop

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ABSTRACT

The dissipation patterns of thiamethoxam insecticide at two different rates (12.5 and 25 μg/g) in both silty clay loam and loam soils were studied. The half lives of thiamethoxam were in the range of 15.0 to 18.8 days in silty clay loam and 20.1 to 21.5 days in loam soil. The residues of thiamethoxam in potato tubers and soil at harvest time (90 days after planting) could not be detected either in soil or in tubers at any of the applied rates (25 and 50 g a.i./ha). Thus, thiamethoxam does not appear to pose any health hazard to consumers or harm to the environment.

Keywords: neonicotinoids; vegetables; recovery; mollisols; half-life; monophasic

Pesticides are considered to be indispensable for the production of adequate grains, fruits and vegetables that are lost due to insects (Atsuko and Toshio 2006). A judicious use of pesticide is essential for management of pests and diseases and productivity of crops (Jeyanthi et al. 2005). The safe use of a pesticide depends on its toxicological properties, persistence as well as the metabolites formed from it. Improper usage of pesticides by farmers often leads to environmental contamination (Barcelo et al. 1994, Lartiges and Garrigues 1995, Vink and Vanderzee 1996). Therefore, a recommendation for the use of any pesticide in a crop grown in an agro-climate cannot be made unless its dissipation/persistence behaviour and adsorption-desorption studies have been ascertained. The information on degradation rate also helps to assess and predict the environmental behavior of the pesticides (Laskowaski et al. 1983).

Thiamethoxam [3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene (nitro) amine] discovered by Ciba (currently, Syngenta) is a new class of second-generation neonicotinoid which has a broad-spectrum insecticidal activity and offers the control of a wide variety of important pests (Maienfisch et al. 2001a,b). Neonicotinoids including thiamethoxam are often used for controlling Colorado potato beetles, potato leafhoppers, potato flea beetles, potato aphids etc. The present investigation was undertaken with the objectives to study the persistence and dissipation behaviours of thiamethoxam in two texturally different soils under laboratory conditions and also to determine the harvest time residues of thiamethoxam in potato tubers in a Typic hapludoll.

MATERIAL AND METHODS

Technical grade thiamethoxam of 98.6% purity was obtained from Syngenta India Ltd. All the chemicals used were of analytical grade (AR) or high performance liquid chromatography (HPLC) grade and were procured from E. Merck or S. D. Fine Chemicals. Only Borosil make glasswares and triple distilled water was used during the study.

Two texturally different surface (0–15 cm) soils belonging to Mollisol order; silty clay loam and loam soil, were collected from the Crop Research

Centre and Practical Crop Production block of the University. Soil samples were dried in shade, crushed with a wooden roller and passed through a sieve having an opening of 2 mm diameter and stored in plastic bags until used for the study. Soil samples were analyzed for their general properties following standard methods (Table 1).

Extraction of thiamethoxam. The extraction of thiamethoxam from soil and potato tubers was done with acetonitrile using water, sodium chloride and anhydrous magnesium sulphate by Quechers (quick, easy, cheap, effective, rugged, and safe) method introduced by Anastassiades et al. (2003).

For extraction of thiamethoxam from the soil samples, 10 g of soil sample was taken in a centrifuge tube of 50 mL capacity and then 5 mL of acetonitrile and 15 mL of water was added to the centrifuge tube. Thereafter, 8 g of anhydrous magnesium sulphate and 7 g of sodium chloride were added to the soil sample. The contents were shaken vigorously for 5 min and then placed on a horizontal shaker at 250 rpm for 1 h. The mixture was centrifuged at 5000 rpm for 5 min. After phase separation, the upper layer of acetonitrile containing extracted thiamethoxam was collected with the help of micropipette without disturbing the lower layer. Thereafter, the cleanup of the extract was done by filtration through a column containing anhydrous sodium sulphate to remove the moisture content. Methanol was used as an eluent. The eluted methanol was dried under the stream of nitrogen and re-dissolved in 1 mL of mobile phase for HPLC analysis. The samples were filtered through 0.45 μm millipore disc filter prior to injection into the HPLC system.

Recovery study. Recovery studies were also carried out in order to establish the reliability of the analytical methods followed above and also know the efficiency of extraction and clean-up steps in the present study. Soil and water samples were fortified with 12.5 and 25.0 μg analytical grade thiamethoxam/g. The samples were extracted and cleaned up following the procedure given in the preceding section.

Half-life of thiamethoxam in soils. Two hundred g of each air dried soil samples were taken in quadruplicate and placed in pre-weighed plastic pot (2.5 kg capacity) and each soil contained in plastic pot was treated with 25 mL of 1000 or 2000 μg thiamethoxam/mL. The contents were thoroughly mixed and left for 2 h for complete evaporation of acetone. The fortified soil was then uniformly mixed with larger remaining 1800 g of each soil with addition of 200 g distilled water to get fortification levels of 12.5 and 25.0 mg thiamethoxam/kg soil. Uniform moisture content was maintained in each pot on alternate days during the period of dissipation study. Ten g soil on oven-dry weight basis was drawn from each pot on 0 (2 h), 1, 3, 5, 7, 10, 15, 21, 28, 35, 45, 60 and 90 days of incubation. The soil samples were extracted for thiamethoxam residues following the procedure described in the preceding paragraphs.

Harvest time residue of thiamethoxam in potato. A micro-plot field experiment was set up in October, 2012 in Plant Physiology Garden. A basal dose of 60 kg N, 43.7 kg P and 83 kg K in form of urea, diammonium phosphate and muriate of potash/ha were uniformly applied to the soil. Three rates of thiamethoxam (0, 25 and 50 g/ha) were applied to soil in five replicates prior to sowing of healthy tubers of potato (cv. Kufri Himalini) with a row to row spacing of 60 cm. The net plot size was (3 m × 3 m). The remaining amount of N fertilizer (60 kg N/ha) was applied at 30 days after sowing. The plots were irrigated as per the requirement. The tubers were harvested in January, 2013. The harvested potato tubers and surface (0–15 cm) soil samples were collected from each plot and brought to the laboratory in plastic bags on the same day for the determination of harvest time residues of thiamethoxam.

Extraction and clean up. The extraction and clean up of thiamethoxam from potato tubers and soil was done using the QuEChERS method as discussed above. In case of extraction from potato tubers, the tubers were finely mashed before extraction and only 10 mL of distilled water was used in the extraction procedure.

Recovery studies from potato tubers. For recovery studies, potato tubers were chopped, mashed and fortified at 12.5 and 25 μg/g levels. The extraction and clean up was carried out as mentioned above and the recovery percentage was calculated.

Table 1. Physicochemical properties of soil

No.	Property	Soil type (depth 0–15 cm)	
1	textural class	Silty clay loam	loam
2	pH	8.16	7.00
3	electrical conductivity (dS/m)	1.130	0.778
4	organic carbon (%)	1.45	1.03

Residue analysis of thiamethoxam. Dionex (Ultimate 3000) HPLC with varying wavelength, UV detector was used for residue analysis. The operating parameters were C-18, 5 μm, (250 × 4.6 mmi.d.) column, mobile phase Acetonitrile: water (90:10) with isocratic mode at a flow rate of 1 mL/min and UV detection of 254 nm. The retention time of thiamethoxam under the above conditions was 2.6 min.

RESULTS AND DISCUSSION

The general properties of the soils are depicted in Table 1. Silty clay loam sample was alkaline in nature with higher organic carbon content and soluble salts (higher electrical conductivity) as compared to loam soil which was neutral.

The recoveries at two fortification levels i.e. 12.5 and 25 μg/g levels ranged between 80.0 ± 1.9 to 82.5 ± 1.1% in silty clay loam and between 85.4 ± 3.2 to 86.6 ± 2.1% in loam soil. The recovery was slightly higher in loam soil due to lower clay and soil organic C contents. In potato tubers, the percent recovery ranged from 82.2 ± 1.2 to 83.5 ± 2.0% at 12.5 and 25 μg/g levels of fortification, respectively.

Dissipation kinetics of thiamethoxam in soil. The amount of thiamethoxam recovered from soil at different time intervals were fitted to a first order kinetic equation:

$$C = C_0 e^{-\lambda t}$$

Where: C – amount of thiamethoxam recovered from soil at time t; C_0 – amount of thiamethoxam recovered at t = 0; λ – degradation constant; t – time (days).

The computed values of coefficient of determination (R^2) for first order dissipation kinetics and half-lives of thiamethoxam under laboratory conditions at two different fortification levels are depicted in Table 2. Highly significant R^2 values indicated that the dissipation of thiamethoxam conformed to the first order kinetics. Soil factors like availability of soil moisture (Gupta 2008), organic carbon content and pH (Karmakar 2006) play an important role in dissipation of pesticides from soil. However, since soil moisture content in the present investigation was maintained to near field capacity so availability of moisture might not be the sole reason for the observed faster dissipation of thiamethoxaam in silty clay loam as compared to loam. Since silty clay loam soil used in the present investigation had higher soil organic carbon content as compared to loam soil therefore, the former soil was likely to maintain higher microbial activity as compared to the latter soil type for effecting higher rate of dissipation. Besides this, an alkaline pH (8.16) of silty clay loam soil could also be an additional factor for faster dissipation of thiamethoxam as compared to loam soil which had a neutral pH (7.0). Thiamethoxam is relatively stable under neutral pH as compared to acidic or alkaline pH (Karmakar 2009). The proposed hydrolytic pathway of thiamethoxam under alkaline condition is affected by the strong electron withdrawing character of the nitro (NO_2) group which could induce a small positive charge (δ+) on the carbon of the cyanide (C≡N) group of the 1,3,5-oxadiazinan-4-ylidene ring thereby initiating the attack of hydroxyl ions.

Harvest time residues of thiamethoxam. No residues of thiamethoxam (< 0.05 μg/g or ND (non detectable)) were detected in potato tubers and experimental soil at harvest time (90 days after planting) at both application rates (25 and 50 g/thiamethoxam). The use of thiamethoxam as an insecticide in potato crop was safe in mollisols and potato tubers from treated fields were also safe for consumption at harvest time (90 days after planting).

Table 2. Calculated values for rate constants involved in degradation kinetics of thiamethoxam at 12.5 and 25 μg/g fortification levels

Parameter	Soil type at 12.5 ppm fortification level		Soil type at 25 ppm fortification level	
	silty clay loam	loam	silty clay loam	loam
λ	0.037	0.035	0.046	0.032242
Half-life ($t_{1/2}$) in days (DT 50)	18.8	20.1	15.1	21.5
Coefficient of determination (R^2)	0.984*	0.984*	0.975*	0.980*
Regression equation	$-0.016x + 0.945$	$-0.015x + 0.982$	$-0.02x + 1.249$	$-0.014x + 1.280$

*$P \leq 0.01$

In conlusion, the dissipation of thiamethoxam from mollisols thus conformed to the first order kinetics and the half-lives were 15.0 to 18.8 days in silty clay loam soil and 20.1 to 21.5 days for loam soil at application rates of 12.5 to 25.0 g thiamethoxam/ha. No detectable residues (< 0.05 μg/g) of thiamethoxam were recorded in soil or potato tubers after 90 days of planting. Hence the use of thiamethoxam in mollisols for potato crop was safe for human consumption and environment.

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