

## **Persistence and Transformation of Thiamethoxam, a Neonicotinoid Insecticide, in Soil of Different Agroclimatic Zones of India**

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Pesticides whether it is a soil applied or applied to foliage invariably reach the soil. Field soils show significant spatial variations in properties, such as organic matter, clay content, bulk density and moisture that can affect the mobility and persistence and thus fate of organic pesticides in the soil environment (Did and Aylmore, 1997). The influence of soil properties along with environmental factors thus plays an important role on the persistence, transformation and efficacy of pesticides (Walker, 1991; Yaduraju et al., 1994; Allen et al., 1995 and Tuxhorn et al., 1997).

The neonicotinoids are emerging as a class of insecticides with novel mode of action and chemistry. They have become established world wide as key components in insect control programme because of their unique properties, such as broad spectrum activity, low use rates, systemic activity, flexible application methods, new mode of action and favourable safety profile (Maienfisch *et al.*, 1999). Thiamethoxam [(*EZ*)-3-(2-chloro-1, 3-thiazol-5-ylmethyl)-5-methyl-1, 3, 5-oxadiazinan-4-ylidene (nitro) amine] (1) is a second-generation neonicotinoid and provides excellent control of important pests such as aphids, jassids, thrips, and whiteflies and lepidopteran pests. Thiamethoxam can be used both for foliar/soil application in most agricultural crops (Antunes-Kenyon and Kennedy, 2001). The compound has recently got registration in India.

The dissipation of first generation neonicotinoid, imidacloprid (Scholz and Spitteller, 1992; Rouchaud et al., 1995 & 1996; Sarkar et al, 2001 and Capri et al., 2001) and second generation neonicotinoid, thiacloprid (Krohn, 2001) in soil were reported but no report is available on the persistence of thiamethoxam in soil. Therefore this study was undertaken to investigate the persistence and transformation of thiamethoxam in four soils of different agroclimatic regions of India.

### **MATERIALS AND METHODS**

Analytical grade thiamethoxam (97.0%) was procured from M/S Syngenta India Ltd. and crystallized from alcohol till constant melting point (139.1°C). Standard solution of thiamethoxam was prepared in acetone and serially diluted to

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get working standards. Soils were collected from four different agroclimatic zones of India. The textural analysis was done with hydrometer method and the organic carbon was estimated with Walkley and Black method. The pH of each soil was measured with pH meter taking soil and water in 1: 2.5 ratio (Jackson, 1973). The texture of the soils was determined by textural triangle chart. The physicochemical properties of different soils are given in Table 1.

**Table1.** Physico-chemical properties of four experimental soils.

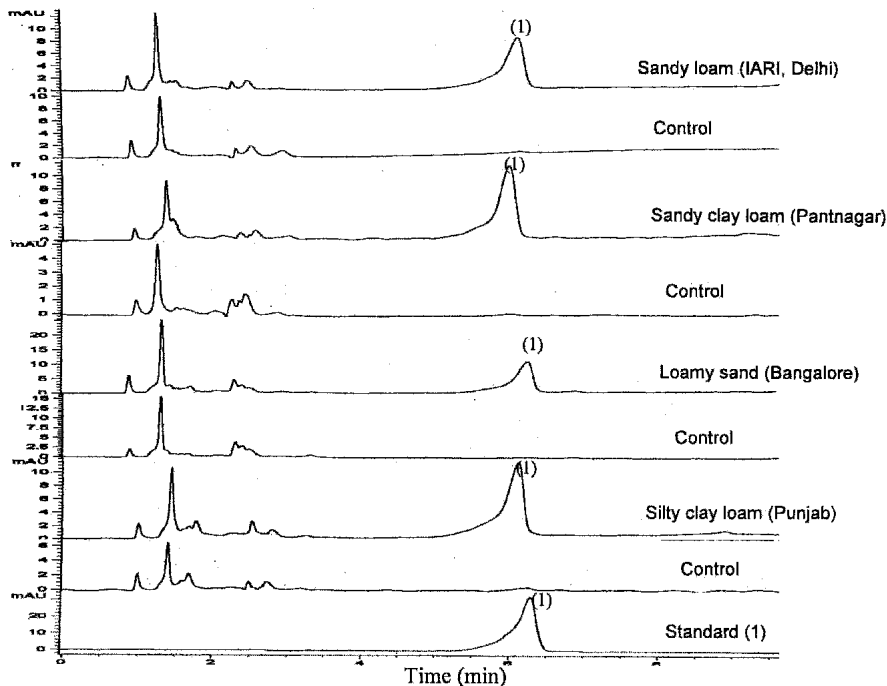
Place of collection	Mechanical analysis				O.C. (%)	pH
	% Clay	% Silt	% Sand	Textural class		
Bangalore	14.61	6.00	79.39	Loamy sand	0.40	6.64
Pantnagar	26.40	22.00	51.60	Sandy clay loam	0.84	7.50
Punjab	30.72	62.00	7.28	Silty clay loam	0.70	8.03
Delhi	17.50	18.70	63.80	Sandy loam	0.50	8.10

O.C. = Organic Carbon

Persistence studies in different soils were carried out in laboratory. Ninety six Erlenmeyer flasks (250 ml) were taken. Sieved and air-dried soil (50g) was taken in each of the triplicate four sets of flasks. Soil samples of seventy two flasks (eighteen flasks for each soil) were fortified at  $1.0 \mu\text{g g}^{-1}$  level with the standard solution of thiamethoxam and mixed thoroughly. An equal volume of acetone was added to control soils. All the flasks along with unfortified control were kept at  $28 \pm 2^\circ\text{C}$  in BOD. The samples (three replicates and one control) were drawn at 0, 5, 10, 15, 20 and 30 days intervals for extraction and analysis.

The samples were brought to the field capacity by the addition of distilled water (1 ml). One hundred millilitre of acetone was added to each flask and mixture was shaken on a horizontal shaker for 30 minutes. The contents of the flasks were allowed to settle and the supernatant phase was filtered through Buchner funnel using water pump. The extraction was done twice more with the same solvent (50 ml each time) and filtered. The combined filtrate was concentrated to around 20 ml on a rotary vacuum evaporator at  $35\text{-}40^\circ\text{C}$ . The concentrated soil extract was transferred to a separatory funnel, diluted with 150 ml saline water (15%) and rinsed by swirling with hexane (30, 20 and 20 ml). The hexane layer was discarded. The aqueous layer was exhaustively partitioned thrice with dichloromethane (30, 20 and 20 ml). The combined organic phase was dried by passing through anhydrous sodium sulphate and evaporated to almost dryness on a rotary vacuum evaporator. The residues were redissolved in acetonitrile for HPLC analysis. An aliquot of the solution was passed through  $>0.45 \mu\text{m}$  filter (13mm dia) prior to injection in HPLC. Recovery of thiamethoxam from four different soils was standardized at 0.5 and  $1.0 \mu\text{g g}^{-1}$  level before starting the experiment to validate the method used for extraction, clean up and analysis.

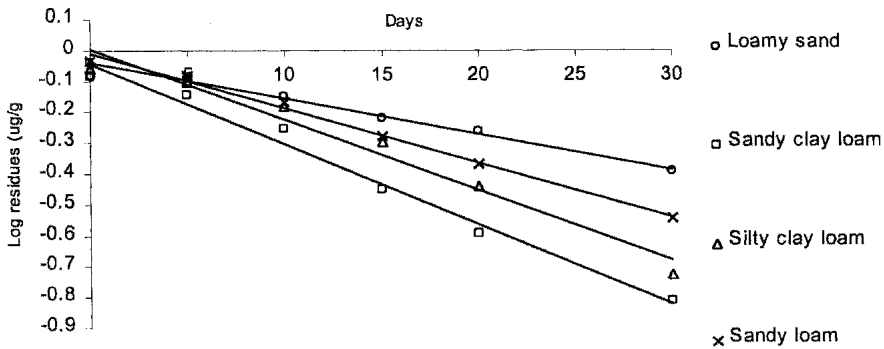
A high performance liquid chromatographic technique was used for the quantitative estimation of thiamethoxam and its degradation / transformation



**Figure 1.** HPLC chromatograms of control and thiamethoxam (1) fortified soils

products. A Hewlett Packard HPLC instrument (series 1100) equipped with a system and a computer (Model Vectra) was used for the analysis of the insecticide and allied products. The stationary phase consisted of Lichrosphere 100 RP-18 packed stainless steel column (250 mm × 4 mm i.d.). The mobile phase was acetonitrile: water gradient maintained at a flow rate of 1.0 ml min<sup>-1</sup>. Gradient programming starting from 85% water: acetonitrile to 60% water: acetonitrile within 10 minutes followed by 10% water: acetonitrile was used (Table 1) for best resolution of thiamethoxam and degradation product (Karmakar et al., 2005). The diode array detector was operated at a wavelength of 254 nm ( $\lambda_{max}$ ). A 20  $\mu$ l aliquot of the sample volume was injected each time and chromatograms recorded in a Windows 95 based HP Chemstation Programme. The amount of thiamethoxam present in each sample was calculated by comparing the area with the standard solution of thiamethoxam (analytical grade).

High performance liquid chromatography-mass spectroscopy (HPLC/MS) was used to identify the degradation product formed in soil. HPLC-MS studies involved an Agilent 1100 series assembled with 1100 series LC/MSD (VWD-G1314A, ALS-G1313A) equipped with binary pump (G-1312A) and degasser (G1379A). The stationary and mobile phases used were same as in HPLC.



**Figure 2.** Linear plot for first order kinetics for dissipation of thiamethoxam from four Indian soils.

## RESULTS AND DISCUSSION

Standard solution of thiamethoxam gave a single sharp peak at 6.3 minute under the described conditions of HPLC. The standard curve was linear from 0.25 to 10.0  $\mu\text{g ml}^{-1}$ . The limit of detection (LOD) was found to be 0.25  $\mu\text{g ml}^{-1}$ . Recovery of thiamethoxam from soil ranged from 85.6 to 90.2%. HPLC analysis of fortified soils showed no interfering peaks (Figure 1). The estimated method detection limit (EMDL) of thiamethoxam from soil using acetone as extracting solvent followed by hexane partition was calculated as 0.03  $\mu\text{g g}^{-1}$ . The limit of quantification was confirmed by fortifying the soils at EMDL level.

Persistence of thiamethoxam was studied in four different soils for 30 days under laboratory conditions. The half life of thiamethoxam in these soils ranged from 11 to 26 days (Table 3). The result showed that initial recovery of insecticide after 5 days did not show much difference in four soils but after that somewhat faster degradation was observed in sandy clay loam soil (32.9%) in comparison of 22-26% in other three soils. A slow dissipation was observed in loamy sand and only 55.7% of thiamethoxam dissipated in 30 days in comparison to 81.6, 78.8 and 69.5% in sandy clay loam, silty clay loam and sandy loam soils respectively. Linear plots of log residues against time showed that dissipation followed a first order rate kinetics (Figure 2).

Loamy sand has acidic pH (6.64) while all other soils are of alkaline pH. Thiamethoxam seems to be relatively stable in acidic soil than in alkaline soil. The fact was also indicated by half life (Table 3) of pesticide in three soils which ranged from 11.5 to 16.9 days in three soils in comparison to 25.5 days in loamy sand (pH 6.64). Percentage of organic carbon was also found to be a responsible factor for dissipation of thiamethoxam in soil. Dissipation was 81.6% in sandy

**Table 2.** Persistence of thiamethoxam in four soils of India

Days after incubation	Average thiamethoxam recovered* $\pm$ S.D.			
	Loamy sand	Sandy clay loam	Silty clay loam	Sandy loam
0	0.909 $\pm$ 0.014 (0)	0.827 $\pm$ 0.015 (0)	0.878 $\pm$ 0.017 (0)	0.924 $\pm$ 0.006 (0)
5	0.806 $\pm$ 0.008 (11.33)	0.713 $\pm$ 0.007 (13.78)	0.787 $\pm$ 0.005 (10.36)	0.826 $\pm$ 0.007 (10.61)
10	0.707 $\pm$ 0.003 (22.22)	0.555 $\pm$ 0.004 (32.89)	0.653 $\pm$ 0.004 (25.63)	0.680 $\pm$ 0.005 (26.41)
15	0.600 $\pm$ 0.005 (33.99)	0.353 $\pm$ 0.005 (57.32)	0.504 $\pm$ 0.004 (42.60)	0.526 $\pm$ 0.003 (43.07)
20	0.543 $\pm$ 0.005 (40.26)	0.252 $\pm$ 0.007 (69.53)	0.361 $\pm$ 0.005 (58.88)	0.424 $\pm$ 0.005 (54.11)
30	0.403 $\pm$ 0.005 (55.67)	0.152 $\pm$ 0.004 (81.62)	0.186 $\pm$ 0.003 (78.82)	0.282 $\pm$ 0.005 (69.48)

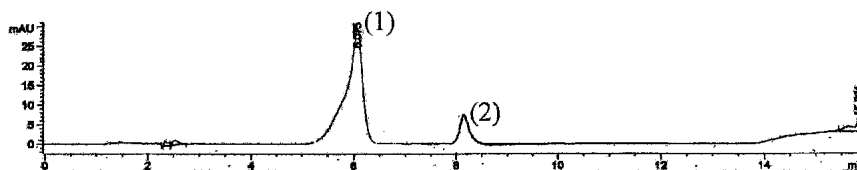
\*Average of three replicates; Figures in the parenthesis shows the % dissipation; S.D. = Standard deviation

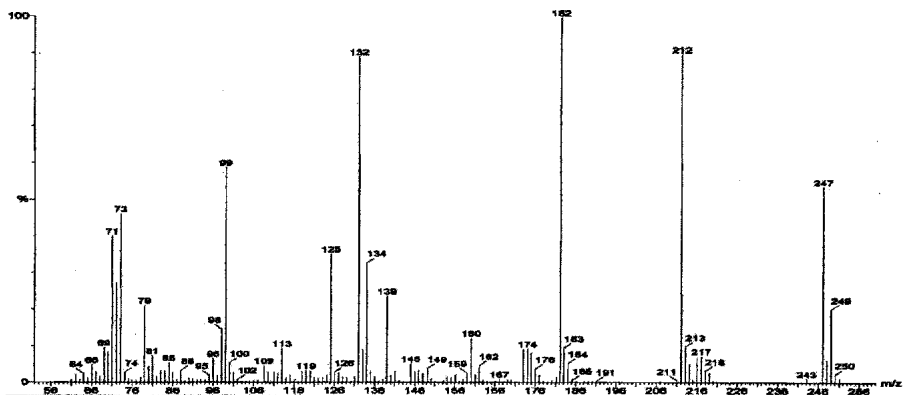
**Table 3.** Regression equations, correlation coefficients and half-life values of thiamethoxam in four soils of India

Soil class	Regression equation	Corre. coeff. ( $r^2$ )	Half-life (days)
Loamy sand	$Y=-0.0118x-0.0373$	-0.99	25.5
Silty clay loam	$Y=-0.0229x+0.0032$	-0.97	13.1
Sandy clay loam	$Y=-0.0261x-0.0448$	-0.98	11.5
Sandy loam	$Y=-0.0178x-0.0099$	-0.99	16.9

clay loam with high organic carbon (0.84%) as compared to loamy sand with low organic carbon percentage (0.4%) where dissipation was only 55.7% in 30 days. Among three alkaline soils fastest dissipation (81.6%) was observed in sandy clay loam which has highest organic carbon content though its pH (7.5) was less than the other two soils. Between the two soils of similar alkaline pH again the dissipation was found to be affected by organic carbon contents when 78.8% dissipation was observed in silty clay loam (0.7% O.C.) in comparison to 69.4% in sandy loam (0.5% O.C.).

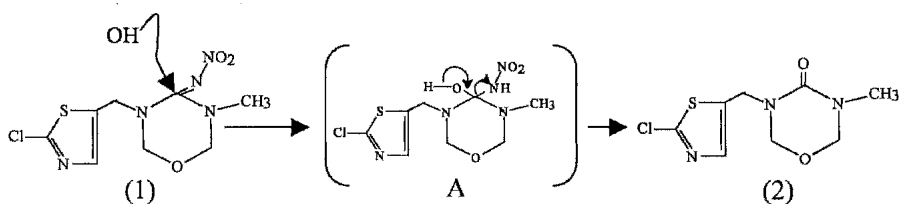
After twenty days HPLC of soil extracts of alkaline pH showed a peak at 8.3 min. (Figure 3) indicating the formation of a degradation product. LC-MS of this peak

**Figure 3.** Thiamethoxam (1) and its degradation product (2) in HPLC Chromatogram of soil after 20 days



**Figure 4.** LC mass of the degradation product (2)

(Figure 4) showed the molecular ion peak at  $m/z = 247$  with fragments at 212 ( $M^+ - Cl$ ); 182 ( $212 - NCH_3$ ) and 132 ( $M^+ - C_4N_4O_3H_7$ ). On the basis of mass spectral data the structure of this compound was assigned as 3-(2-chloro-1, 3-thiazol-5-ylmethyl) 5-methyl-1, 3, 5-oxadiazin-4-one (2, Figure 5). A plausible mechanism for formation of compound 2 from thiamethoxam under alkaline pH has been proposed via intermediate A (Figure 5).



**Figure 5.** A plausible mechanism for the formation of degradation product (2) from thiamethoxam (1) via an intermediate (A)

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