

Leaching Behaviour of Ready-mix formulation of (Chlorantraniliprole 8.8 % + Thiamethoxam 17.5 % SC) at different Depths of Sandy Loam Soil

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ABSTRACT: Ground-water pollution through leaching of pesticides is one of the major issues. This in turn results in hazard to aquatic systems and drinking water resources. Diffused chemicals via leaching make groundwater vulnerable to pollution, hence making it unfit for proper usage. So, in order to safeguard the leaching losses as well pattern of diffusion, leaching behaviour of ready-premix formulation of Chlorantraniliprole 8.8% + Thiamethoxam 17.5% SC was experimented in sandy loam soil at 150 g. a.i. ha⁻¹ (single dose) and 300 g a.i. ha⁻¹ (double dose) under various laboratory conditions following average annual rainfall of 400 mm. Residues were estimated at variable depths of soil and in leachates with the help of gas chromatography (GC-MS) equipped with electron capture detector (ECD). Method validation was done by performing recovery procedures at a series of different spiking levels ranging 0.01 - 0.10 mg kg⁻¹. Results obtained reported that the residues retained maximum in uppermost core i.e. 0 - 5 cm layer of soil with 79.53 and 85.57 per cent retention for both chlorantraniliprole and thiamethoxam while residues reached below detectable level of 0.01 mg kg⁻¹ after 20 cm depth of soil at both doses. Since, no residues of combination product were observed in any leachate fraction. Hence, this combination product can be regarded safe for soil and ground water contamination.

Keywords: Diffusion, leaching, method, pesticide, wet.

INTRODUCTION

Ground water as well as surface water deterioration and contamination all around the globe has come up as a fire point over the last few decades due to extent use of pesticides. Residues of a number of pesticides and their degradation products have been very frequently detected in water collected from fields and irrigation canals. On one hand these agro-chemicals are one of the major agricultural assets these days, but whether used in natural or synthetic form, they do actively pose innumerable toxicological hazards and can cause severe risks if occur as remains in the environment. Their persistence as well as leaching in soil contributes huge towards groundwater contamination. There are a number of factors that signifies the presence of insecticide residues in runoff, sediment and leachate, and their mobility or persistence in soil. Such factors include, chemical and physical properties of the compound, soil properties, rainfall, bed construction and the degree of slope (Halimah *et al.*, 2005). With the

uncontrolled use of these agricultural chemicals are associated many problems like persistence of residual toxicants in the ecosystem, insect resistance and resurgence. Soil is one of the most important components of the ecosystem, as it is the base to flora as well as micro- fauna. Also, as it acts as a sink for all the inputs used in agriculture including pesticides. But as the pesticide remains in bound forms these in turn halt the growth as well as well-being of microflora and hence affect soil properties. Also, these bound residues in soil can be a source of contamination for succeeding crop too. These chemicals from soil further reach the water bodies by leaching and runoff. Other than this the major processes that inherently condition the eventual fate of various pesticides in soil include, retention by soil materials (adsorption/desorption processes), transformation processes (biological and chemical degradation) and transport (via soil, atmosphere, surface water, or ground water) (Dagar *et al.*, 2014). Now-a-days an alternative approach to cover the wide as well as complex spectrum of the pest is to make

formulation with suitable combination of insecticides. These pre-mix combination formulations can be applied as foliar, seed dressers and as soil drench. One such similar ready-pre mix formulation is Volium Flexi (8.8% chlorantraniliprole + 17.5% thiamethoxam) recommended as soil drench. These two insecticides individually or in mixtures, have been experimented and observed very efficient to check insect pest population.

Chlorantraniliprole [3-bromo-N- [4-chloro-2-methyl-6-[(methyl amino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl) - 1H-pyrazole-5-carboxamide] is an anthranilic diamide insecticide developed by Dupont Crop Protection, 2007 is used as an active ingredient of many different formulations. It has also been reported that this mixed formulation amalgamates each other to combat the toughest insects in vegetables that includes a wide range of lepidopteron pests, aphids, whiteflies and flea beetles (Oliveira *et al.*, 2001). Chlorantraniliprole acts by activating the uncontrolled release of internal calcium stores, which leads to Ca^{2+} depletion, feeding cessation, lethargy, muscle paralysis, and finally insect death (Lai *et al.*, 2011; Cordova *et al.*, 2006). Neonicotinoid, thiamethoxam, (EZ)-3-(2-chloro-1, 3-thiazol-5-ylmethyl) - 5-methyl-1, 3, 5-oxadiazinan-4-ylidene (nitro) amine, is an N-substituted neonicotinoid that acts agonistically on nicotinic acetylcholine receptors (nAChR). The compound interrupts in the process of information transfer between nerve cells by interfering with nicotinic acetylcholine receptors in the CNS, this blockage leads to the accumulation of acetylcholine resulting in the insect muscle paralysis and eventually leading to death. Thiamethoxam is observed to be mobile while chlorantraniliprole slightly mobile. Borsuah *et al.* (2020). Present study focuses on their combined mobility and the pattern of leaching.

As large amounts of many different pesticides are used globally, they and their degradation products can sometimes pollute groundwater at unacceptable levels. Indeed, diffuse pollution by pesticides has become a major soil threat (Stolte *et al.*, 2016; Silva *et al.*, 2019). For this reason that assessment of transport pattern as well as soil mobility of pesticides is required and is one indispensable element that regulators use to assess probable pesticide safety (Katagi, 2103). Ground water is the point source for drinking and irrigation water so it is necessary to assess the risk of ground water contamination by both the insecticides. Also, very limited research work and literature is available on the leaching pattern of the combination formulation, being used widely. With the same concern preset experiment was carried out to study the leaching behavior of both the insecticides used in the combination product in sandy loam soil at different doses under laboratory conditions.

MATERIALS AND METHODS

Leaching studies of combination product Chlorantraniliprole + Thiamethoxam in soil were carried out under laboratory conditions during March-June, 2018. The experiment was conducted with sandy loam soil collected from Research Farm of CCS HAU, Hisar. All the physio-chemical properties of the soil are given in Table 1.

Table 1: Physico-chemical characteristics of soil.

Parameter	Value
Soil Type	Sandy loam
pH	7.6
EC ($dS\ m^{-1}$)	2.0
O.C. (per cent)	0.68
P_2O_5 ($kg\ ha^{-1}$)	14

Packing of glass column. Plexi glass columns of dimensions 90 cm × 2.2 cm I.D., fitted with perforated plexi glass sieve covered with Whatman No. 1 filter paper at the bottom was used for the leaching experiment. Seven columns were packed (three replicates of SD and DD each and one control) with soil up to 60 cm height to a uniform bulk density (BD) of $1.35\ g\ cm^{-3}$. Pre-weighed soil was added to the columns every time via a funnel and tapping gently, repeating till each column packed upto 40 cm. All the columns were covered with filter paper and were finally installed on stands with bottles to collect eluents during leaching.

Triplicates of each dose were installed on to carry out the leaching studies. 5g soil was fortified with SD and DD solution of ready- mix formulation and was poured from the top of the column. One control column packed with soil only was installed to which no pesticide was added. All the soil columns prepared were subjected to leaching with 50 mm of water at a time. 50 mm lot of water i.e. 18.9 ml was added, avoiding any spattering of soil. The procedure was repeated with the next 50 mm lot of water 24 hours after observing no standing water in the columns. Leaching was repeated till 400 mm depth, avoiding evaporation losses by covering with perforated polythene bags. After 400mm depth leaching, all the soil sections were taken out and were sorted into pieces of 5 cm each. All these pieces were shade dried, grinded and sieved and analyses for quantification of ready-pre-mix formulation (chlorantraniliprole + thiamethoxam) residues. Leachates eluted of the columns were collected and processed further to check for the presence of ready-pre-mix formulation (chlorantraniliprole + thiamethoxam) residues.

Extraction and clean up. As soon as the leaching was complete, intact soil cores were taken out of each column.

Each of the core was sliced into individual pieces of height 10 cm each and were air dried, ground and sieved through a 2 mm sieve for further analysis. Leachates collected of all the columns were pooled and processed to check the presence of combination product (Chlorantraniliprole + Thiamethoxam) residues. Water extract were processed by liquid-liquid partitioning and finally analysed on GC-MS\MS analysis.

RESULTS AND DISCUSSION

Leaching behaviour of Chlorantraniliprole. The data regarding the leaching behaviour of chlorantraniliprole in soil at single and double dose is presented in Table 2 and 3. In SD, the residues retained maximum in first section of soil with 79.53 per cent retention. Comparatively very less leaching was observed in next soil sections *i.e.* 5 - 10 cm with 7.76 per cent while 10-15 cm section showed up only 1.91 per cent retention. Total 89.20 per cent of chlorantraniliprole was recovered at SD. Total retention at DD was observed to be 92.08 per cent. 81.56 per cent leaching was observed in the first soil core and in further sections *i.e.* 5-10 and 10-15 cm only 8.41 and 2.11 per cent retention was observed, respectively.

Leaching behaviour of Thiamethoxam. In SD, the residues retained maximum in uppermost core *i.e.* 0 - 5 cm layer of soil with 85.57 per cent retention. Comparatively very less leaching was observed in next soil sections *i.e.* 5-10 cm with 9.66 per cent while 10-15 cm section showed up only 2.81 per cent retention. Total 98.08 per cent of thiamethoxam was recovered at single dose. For DD of thiamethoxam, 83.54 per cent leaching was observed in the first soil core *i.e.* 0-5 cm. In further sections the leaching per cent was very less *i.e.* 10.15 (5-10 cm), 2.11(10-15 cm) and only 0.91 (15-20 cm) per cent retention was observed, respectively. Total retention at D was observed to be 96.71 per cent. Very similar leaching per cent of thiamethoxam was observed by Kurwadkar *et al.* (2014) in leaching capability of thiamethoxam in soil of vineyard along

Dinotefuran and Imidacloprid. Mass leached from the column, with percent recovery were Imidacloprid (69.92 per cent) < Dinotefuran (79.12 per cent) < Thiamethoxam (81.67 per cent). The trend in leaching potential was attributed to their water solubility. Thiamethoxam is highly water soluble, because of its higher solubility, have low tendency of being sorbed to the soil material thereby increasing leaching ability. Anita *et al.* (2019) also worked on leaching pattern of indoxacarb in sandy loam soil at two doses. A total of 93.48 and 88.98 per cent out of 2.77 and 5.54 $\mu\text{g g}^{-1}$ indoxacarb was recovered from SD and DD, respectively. Similar to our study, all the leachate fractions from both the treatments were free from indoxacarb residues. From the present findings of both chlorantraniliprole and thiamethoxam, maximum retention in uppermost layer and no residues in leachates suggests that it would not leach to groundwater bodies therefore do not cause water pollution. Results were also in alliance with those of Das *et al.*, (2012) who studied downward movement of flubendamide in soil All the leachate fractions were free from flubendamide residues. Residue per cent retention were 60.05 and 80.93 per cent recovered out of initial 20 μg added flubendamide in soil. Flubendamide per cent distribution of at different depths (0-5, 5-10, 10-15, 15-20 and 20-25 cm) was 19.51, 68.06, 9.14, 1.95 and 0 respectively and in 39.35 SC formulation was 67.22, 28.62, 2.31, 1.85 and 0 respectively. The results depicted those formulations declined the downward movement of flubendamide in soil column. Spomer *et al.* (2011), in a soil leaching study reported that for chlorantraniliprole, few data indicated greater downward diffusion in sandy loam soil, with about 90% of the applied pesticide remaining in the top 5 cm layer of the soil columns. Few other studies too depicted half-lives of chlorantraniliprole in the range of 4 and 22 in different soils (Malhat *et al.*, 2012; Sharma *et al.*, 2014; He *et al.*, 2016; Ramasubramanian *et al.*, 2016).

Table 2: Leaching behaviour of Chlorantraniliprole and Thiamethoxam in sandy loam soil and in leachates at single dose.

Soil depth (cm)	Chlorantraniliprole		Thiamethoxam	
	Residues (μg)* \pm SD	% Retention	Residues (μg)* \pm SD	% Retention
0-5	0.41 \pm 0.03	79.53	0.595 \pm 0.28	85.57
5-10	0.351 \pm 0.02	7.76 0	0.582 \pm 0.06	9.66
10-15	0.040 \pm 0.03	1.91	0.143 \pm 0.03	2.81
15-20	BDL	BDL	BDL	BDL
20-25	-	-	-	-
25-30	-	-	-	-
Leachate	-	-	-	-
Total recovered		89.20		98.08

*Average residues of three replicates

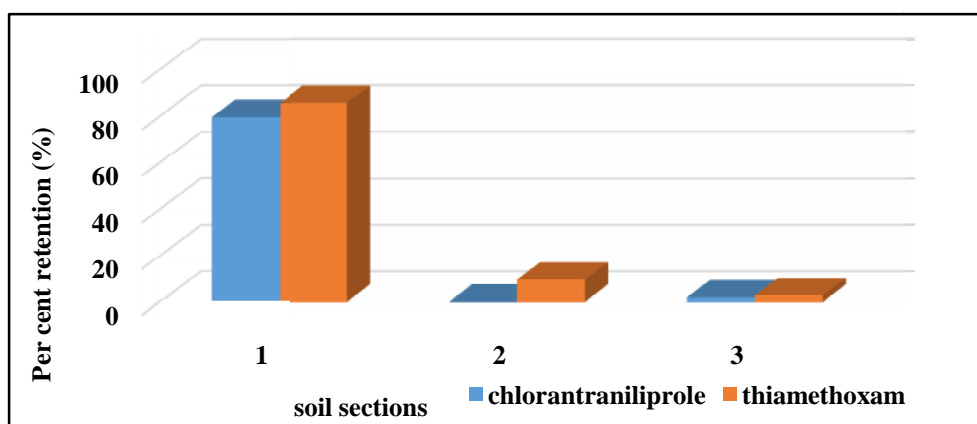


Fig. 1. Distribution of chlorantraniliprole and thiamethoxam residues at different soil depths at single doses.

Table 2: Leaching behaviour of chlorantraniliprole and thiamethoxam in sandy loam soil and in leachates at double dose.

Soil depth (cm)	Chlorantraniliprole		Thiamethoxam	
	Residues (μg)* \pm SD	% Retention	Residues (μg)* \pm SD	% Retention
0-5	0.71 \pm 0.03	81.56	1.436 \pm 0.28	83.54
5-10	0.091 \pm 0.02	8.41	1.120 \pm 0.06	10.15
10-15	0.021 \pm 0.03	2.11	0.146 \pm 0.03	2.11
15-20	BDL	BDL	0.030 \pm 0.02	0.91
20-25	-	-	BDL	BDL
25-30	-	-	-	-
Leachate	-	-	-	-
Total recovered		92.08		96.68

*Average residues of three replicates

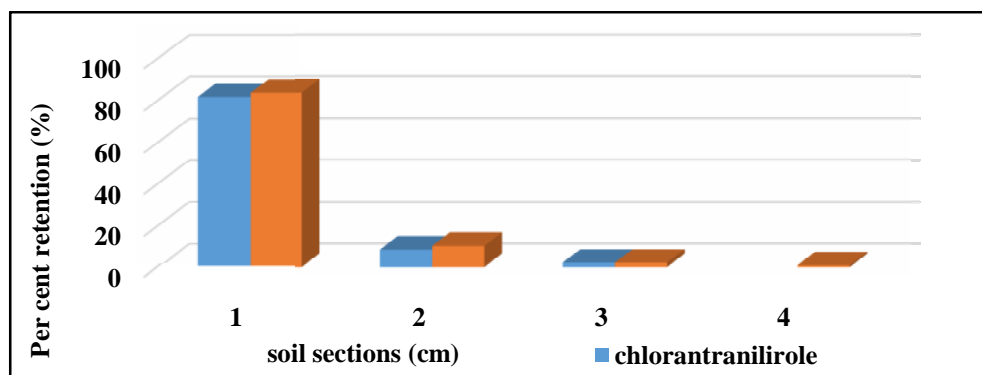


Fig. 2. Distribution of chlorantraniliprole and thiamethoxam residues at different soil depths at double doses.

CONCLUSIONS

The present experiment was conducted in order to ensure safety, sensible as well as effective use of the insecticides Chlorantraniliprole and Thiamethoxam with respect to human health risks and ecology safety. From the results discussed it can be concluded that no residues were present after 40 cm depth in both the cases and none of the residues of combination product were observed in leachates, hence it is safe for both soil as well as ground water. With the obtained results the scope for risk arising from future use of the combination product is ensured and are safe for use.

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Conflict of Interest. None.

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