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Assessing the degradation pattern of ready pre-mix formulation of chlorantraniliprole + thiamethoxam in canal water under laboratory conditions

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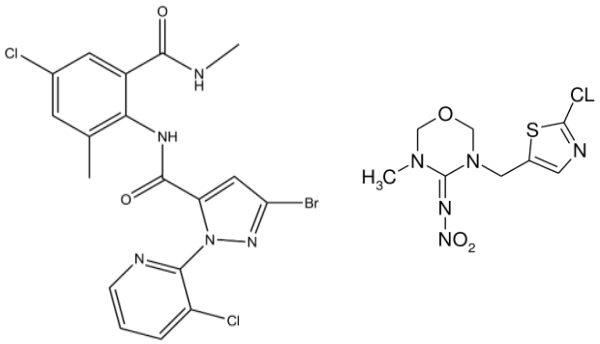
Abstract
The global use of pesticides in agricultural and non-agricultural sectors has out-turned in the presence of mammoth residues in a variety of environmental commodities including plants, soil and water resources. Contamination of water takes place not only with the on-going use of agrochemicals but additionally due to leaching of persistent chemical ingredients from soil. A laboratory experiment was conducted during the year 2019, at CCS Haryana agricultural university, Hisar, Haryana in order to estimate the decline in levels of ready pre-mix formulation of Chlorantraniliprole + Thiomethoxam in canal water. Ready pre-mix formulation of Chlorantraniliprole + Thiomethoxam (Volium Flexi) was mixed in the canal water samples collected in amber bottles at the rate of 0.0375µg mL^{-1} (SD) and 0.750µg mL^{-1} (DD). Samples were collected on 0 (1 h), 3, 5, 7, 10, 20, 30, 45, 60 and 90 days after spiking. The technique of liquid-liquid partitioning with DCM (dichloromethane) was used for processing the collected water samples. Finally, the residues were estimated using GC MS/MS.

Keywords: Chlorantraniliprole, canal water, pesticide, residues, thiamethoxam, photo degradation

Introduction
The term "pesticide" is an amalgam phrase that covers all the chemicals used to kill or control pests. They have a great role in food production and are used as crop protectants against insects, fungi, rodents, nematodes and many other pests. In agriculture perspective, the term pesticide generally includes herbicides, insecticides, fungicides, algaecides, nematocides, and rodenticides. pesticide residues are being reported as common organic contaminants worldwide in surface waters and other environmental matrices (Gilliom *et al*., 2007; Rathode *et al.*, 2012; Ali *et al.*, 2014) [8, 10].
Neonicotinoid and Anthranilicdiamide chemical groups of insecticides are the major emerging plant protectant these days. Thiamethoxam [3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene (nitro) amine] is a potent systemic insecticide of the rapidly growing class, Neonicotinoids **(**neuro-active insecticides chemically similar to nicotine). Analogous to nicotine, their mode of action is by binding to nerve cell receptors responding to the neurotransmitter acetylcholine. It has slight acute toxicity (LD_{50} 1530 mgkg"1 to rats) and fall under toxicity category III in acute oral and dermal studies. (Pooja *et al.*, 2021) [7]. Generally, neonicotinoids have a selective action on the central nervous system of insects. Additionally, these have nominal effects on valuable insects and low mammalian toxicity, without prompting either teratogenic or mutagenic effects. Thiamethoxam acts effectively against many sucking and biting insects, like aphids, whiteflies, etc. it can be applied as foliar spray in plants as well as to the seeds. Another dynamic systemic insecticide, Chlorantraniliprole {3-bromo-N-[4-chloro-2-methyl-6- [(methylamino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)- 1H-pyrazole-5-carboxamide} belongs to the class anthranilic-diamide, which is widely used for lepidopteran coleopteran, and some dipteran pest control. The mode of action is selective binding to ryanodine receptors (RyR) present in insect muscles. This in turn results in imbalanced release of calcium in the sarcoplasmic reticulum[1], causing impaired regulation of muscle contraction and leading to feeding cessation, lethargy, paralysis, and eventual death of target organisms[2] (Lai *et al.*, 2011) [4]. Also, it is a remarkable point that very little toxicity to non-targeted organisms like mammals, birds, fishes etc. is observed with chlorantraniliprole.
Besides various benefits, these agrochemicals do pose numerous ill effects to the environment and its organisms, when not used in accordance with the recommended doses.

In humans, there are innumerable evidences of acute as well as chronic poisoning based upon the extent of exposure to them. In environment, these may remain in soil and water for long periods causing harm to different organisms. In soil these may occur as bound residues which alter with plant growth and development. Also, their presence in aquatic bodies causes toxicity to the aquatic zooplanktons and phytoplankton. Their presence in water makes the water unfit for agricultural and human use. From irrigation water, these indirectly leach into the soil and are generally taken up by plants and finally by us.

Nature and solubility of pesticide, microbial activity, soil temperature, Phyto degradation and rainfall are some of the factors that affect the pollution of water by pesticides. Keeping in mind the ill effects, the present study was designed with the aim to assess the effect of photo-degradation of ready pre-mix formulation of Chlorantraniliprole + Thiamethoxam in irrigation Canal Water under Laboratory Conditions.



Chlorantraniliprole Thiamethoxam

Fig 1: Structure of chlorantraniliprole and thiomethoxam.

Material and Methods

Thiamethoxam, chlorantraniliprole samples, glassware and solvents

Ready-mix formulation of Chlorantraniliprole + Thiamethoxam (Volium Flexi) was purchased from local market of Hisar, Haryana. A 100ppm standard stock solution was prepared in acetone and diluted in series (2.00, 1.50, 1.00, 0.50, 0.25, 0.10 and 0.05 µg mL^{-1}) in order to establish a calibration curve. All the solutions prepared were stored at 4˚C. Analytically graded solvents were used. All the glassware required was washed thoroughly and rinsed with distilled water in order to keep away any contamination.

Instruments

GC-MS/MS Shimadzu Model GCMSTQ-8040, equipped with split/Split less injection port and auto sampler (Shimadzu AOC 20S) coupled with triple quadruple mass spectrometer (TQMS) was used to carry out the chromatographic separations. The column used was SH-Rxi-5 Sil MS (30 m x 0.25 mm x 0.25 µm film thickness). Oven temperatures ranges were 80 (2 min), 200C min^{-1}, 180 (0 min), 50C min^{-1}, 3000 (3 min). Ion source temperature and injection port temperature were 200^0C and 250^0C respectively. All other necessary parameters of the instrument are provided in the Table. 1.

Table 1: GC MS/MS parameters

Carrier gas	Helium
Through column	1.46 ml min^{-1}
Total flow	21 ml min^{-1}
Split ratio	Splitless
Limit of quantification (LOQ)	0.01 µg/kg
Limit of detection (LOD)	0.005 µg/kg
Retention time (R_t)	13.7
	20.4
Injection mode	Autoinjector Split less

Laboratory experiment/trials

The laboratory experiments were carried out from June to October 2019 in Pesticide Residue Laboratory, department of Entomology, CCS HAU, Hisar. Water samples of 500ml were collected in 37 (36 treated + 1 control) clear bottles from the canal, in two replicates and were treated with ready-mix formulation of Chlorantraniliprole + Thiamethoxam (Volium Flexi) at the rate of 0.0375 µg ml^{-1} (SD) and 0.0750 µg mL^{-1} (DD). Control sample was left as such. All the bottles along with control were kept in open where a regular exposure of sunlight was available. Sampling for estimation of residues were performed on 0 (I h), 3, 5, 10, 20, 30, 45, 60 and 90 days after treatment. The physico-chemical characteristics of canal water are provided in Table. 2

Table 2: Physico-chemical characteristics of canal water

EC $10x^6$ (µ sm^{-1})	240
HCO_3 (mel^{-1})	0.42
Ca^{+2} (mel^{-1})	1.1
Mg^{+2}(mel^{-1})	2.7
pH	8

Extraction and clean-up

For extraction and clean-up, the method of Buttler and Thorstensen and Lode was followed with some modification. Water samples were taken regularly in accordance to the days mentioned above and transferred into a separatory funnel and added 50 g sodium chloride. Then, partitioning was performed thrice using DCM (dichloromethane) (50, 25, 25

mL), collecting the lower organic layer each time in a 500mL conical flask, by passing through a bed of Na_2SO_4. Extract in the conical flask was then concentrated on a Rotary Evaporator till near dryness. Final volume of 3 mL was prepared with n-hexane for performing GC-MS/MS analysis.

Results and Discussion

1. Recovery studies

Recovery experiments were performed before conducting the experiment. water samples were spiked with Volium Flexi at three concentration levels @ 0.01, 0.10, 0.25µg g^{-1}. The reported results were mean of all the replicates at each spiked level. The limit of quantification (LOQ) and detection (LOD) 0.01 and 0.005 µg ml^{-1}, respectively. It is well observable from the Table. 3, below that the per cent recovery values of chlorantraniliprole and thiamethoxam insecticide from water with liquid-liquid partitioning were very satisfactory as all the values were above 80 per cent. The respective recoveries ranged from 81.00-84.74 and 82.76-89.75 per cent for chlorantraniliprole and thiamethoxam, respectively.

Table 3: Percent recovery of Chlorantraniliprole and Thiamethoxam insecticide from water using liquid-liquid partitioning.

Fortification levels (µg g^{-1})	Replicates	Chlorantraniliprole		Thiamethoxam	
		Recovery (%)	Average* Recovery (%) ± SD	Recovery (%)	Average* Recovery (%) ± SD
0.01	R_1	80.41	81.00 ± 0.59	82.78	82.76 ± 0.40
	R_2	80.78		82.25	
	R_3	81.82		83.25	
0.10	R_1	83.21	83.59 ± 0.38	87.56	88.31 ± 0.63
	R_2	84.12		88.26	
	R_3	83.45		89.12	
0.25	R_1	85.21	84.74 ± 0.37	89.25	89.75 ± 1.23
	R_2	84.73		88.56	
	R_3	84.28		91.45	

*Average of three replicates

2. Residues in water

Table 4 and Figure 2 below presents the data showing the dissipation pattern of chlorantraniliprole residues in water system at single and double dose. It is clearly, examined that the initial average concentration was 0.146 and 0.32 at single and double doses respectively. Residues dissipated up to 30 days at single dose with average values of 0.146, 0.134, 0.118, 0.015, 0.095, 0.084, 0.058 and 0.24, while for double dose the residues persisted up to 45 days after treatment with 0.32, 0.2, 0.27, 0.214, 0.198, 0.178, 0.167, 0.097 and 0.06 average values. The per cent dissipations ranged as 13.04, 32.06, 41.30, 47.8, 54.34, 76.0888.22, 19.18, 28.08, 34.98, 42.47, 60.27, and 83.56 at single dose while for double dose 12.50, 15.63, 33.13, 38.13, 44.38, 47.81, 69.69 and 81.25 per cent dissipation was observed.

Table 4: Persistence of residues of chlorantraniliprole insecticide in irrigation water system at single and double dose

Days after treatment	Chlorantraniliprole residues (mg kg^{-1})			
	T_1 (150 g a.i. ha^{-1})		T_2 (300 g a.i. ha^{-1})	
	Average residues* ± SD	% Dissipation	Average residues* ± SD	% Dissipation
0	0.146	-	0.32	-
1	0.134	8.22	0.28	12.50
3	0.118	19.18	0.27	15.63
5	0.105	28.08	0.214	33.13
7	0.095	34.98	0.198	38.13
10	0.084	42.47	0.178	44.38
.20	0.058	60.27	0.167	47.81
30	0.024	83.56	0.097	69.69
45	LOQ		0.06	81.25
60			LOQ	
	Correlation Coefficient R^2 = 0.9981 Regression Equation y = - 0.0259x + 1.1582 $t_{1/2}$ = 12.4 days		Correlation Coefficient R^2 = 0.9764 Regression Equation y = 0.0153x + 1.4465 $t_{1/2}$ = 19.06 days	

*Average residues ± SD of three replicates; BDL: <.01 mg kg^{-1} for regression equation, [Residues (mg kg^{-1}) x 10^3] is taken.

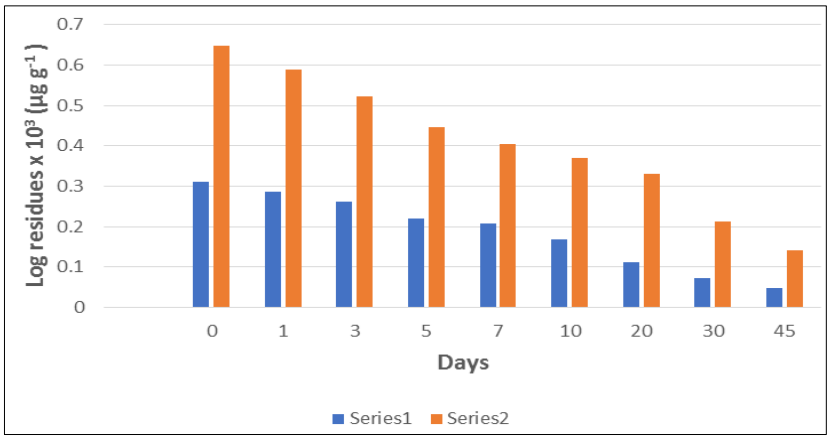


Fig 2: Degradation kinetics of chlorantraniliprole in water system at single and double dose

Data relating to the dissipation pattern of thiamethoxam residues in water system at respective single and double dose is presented in Table 5 and Figure 3. It is clearly, reported that the initial average concentration was 0.31 and 0.649 at single and double doses respectively. Residues persisted up to 45 days at single dose with average values of 0.31, 0.286, 0.262, 0.219, 0.207, 0.169, 0.111, 0.072, and 0.048 while for double dose the residues persisted up to 60 days after treatment with, 0.649, 0.589, 0.523, 0.446, 0.405, 0.371, 0.331, 0.212, 0.141 and 0.073 average values. The per cent dissipations ranged as 7.74, 15.48, 29.35, 33.20, 45.48, 64.19, 76.77 and 84.51 at single dose while for double dose 9.24, 19.41, 31.28, 37.60, 42.84, 49.00, 67.33, 78.27 and 88.75 per cent dissipation was observed.

Table 5: Persistence of residues of Thiamethoxam insecticide in irrigation water system at single and double dose

Days after treatment	Thiamethoxam residues (µg kg^{-1})			
	T_1 (150 g a.i. ha^{-1})		T_2 (300 g a.i. ha^{-1})	
	Average residues* ± SD	% Dissipation	Average residues* ± SD	% Dissipation
0	0.31	-	0.649	-
1	0.286	7.74	0.589	9.24
3	0.262	15.48	0.523	19.41
5	0.219	29.35	0.446	31.28
7	0.207	33.20	0.405	37.60
10	0.169	45.48	0.371	42.84
20	0.111	64.19	0.331	49.00
30	0.072	76.77	0.212	67.33
45	0.048	84.51	0.141	78.27
60	LOQ	-	0.073	88.75
90			LOQ	
	Correlation Coefficient R^2 = 0.9611 Regression Equation y = -0.0221x + 1.4721 $t_{1/2}$ = 13.60 days		Correlation Coefficient R^2 = 0.9823 Regression Equation y = 0.0166x + 1.7792 $t_{1/2}$ = 18.01 days	

*Average residues of three replicates.

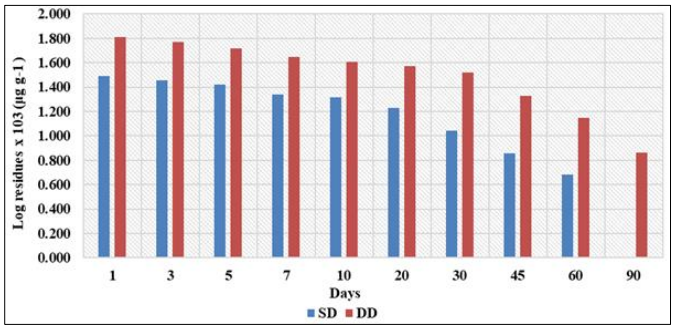


Fig. 3: Degradation kinetics of thiamethoxam in water system at single and double dose

The results presented were aligned with those of Chauhan *et al.*, (2008) who performed laboratory study on the degradation of propiconazole in water system by liquid-liquid partitioning. All the recoveries were reported to be above 90 percent. 0.059 And 0.119 µg g^{-1} were the initial deposits reported on 0 (2 hours) day at SD and DD, respectively. The residues dissipated up to 90 (0.010) and (0.022) days with per cent 83.20 and 81.50 dissipation for SD and DD, respectively. Correlation coefficient (r^2) was observed to be 0.98. The residues at both the treatments dissipated quickly up to 7 days in canal water followed by slow dissipation up to 30 days and the dissipation further slowed down in both the applications reporting dissipation of about 80 per cent in 90 days. The respective $t_{1/2}$ values were 35.8 and 38.2 days for single and double dose.

Conclusions

The above said experiment was conducted in order to safeguard the sensible as well as effective use of the insecticide Chlorantraniliprole and Thiamethoxam with respect to human health risks and environmental safety. The dissipation pattern of chlorantraniliprole + thiamethoxam in water was examined by collecting water from the canal nearby in transparent white plastic bottles (water + ready pre-mix formulation of chlorantraniliprole + thiamethoxam) of 500 mL each. Processing was done in laboratory by liquid-liquid partitioning. Both the insecticides reach below quantification level in water, so are safe for use and do not contaminate the water table.

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Figure: Structure of chlorantraniliprole and thiamethoxam.

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