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

Pooja, Sushil, Preeti Dhanker and Reena Chauhan

Abstract
The global use of pesticides in agricultural and non-agricultural sectors has out-turned in the presence of mammoth residues in a wide variety of environmental commodities including plants, soil, and water resources. Contamination of water takes place not only with the ongoing use of agrochemicals but in addition to this due to the leaching of persistent chemical ingredients from the soil. A laboratory experiment was conducted during the year 2018-2019, at Chaudhary Charan Singh Haryana agricultural university, Hisar, Haryana in order to estimate the decline in levels of ready pre-mix formulation of thiamethoxam + lambda - cyhalothrin in canal water. Ready pre-mix formulation of thiamethoxam + lambda - cyhalothrin (Alika) was mixed in the canal water samples collected in amber bottles at the rate of 0.5 µg mL^{-1} (Single Dose, SD) and 1 µg mL^{-1} (Double Dose, DD). Water samples were collected on 0 (1 h), 3, 5, 10, 20, 30, 45, 60, and 90 days after spray application. 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: Pesticide residues, thiamethoxam, lambda - cyhalothrin, photo-degradation canal water, photo degradation

Introduction

The agricultural sector plays a strategic role in the process of economic development of the country. Our country is totally an agriculture-dependent country, with a major role as producer as well as exporter. The country has approximately 20 percent contribution to the GDP (gross domestic product). As per the data analyzed in the year 2016, agriculture and all other allied sectors including animal husbandry fisheries as well as forestry have accounted for approximately 15.4 per cent of the GDP with about 41.49 per cent of the workforce in 2020. Being a well factual exporter, the total agriculture commodities exported by our nation was the US $3.50 billion in March - June 2020. The country exported a lump sum amount of $38 billion worth of agricultural products in 2013, making it the 7th largest agricultural exporter globally and the 6th largest net exporter (USDA, 2014).

Hunger and production moved parallelly, but at this time, with the development of innumerable as well as efficient ways of crop production, the big issue of hunger can be left behind. Food security has been described as a condition of humanity "...when all people, at all times, have physical and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life." (Food and Agriculture Organization 1996) [25]. Agricultural development policies in our countries have been a great backhand and have reduced hunger and food insecurity at a very rapid rate. The use of agricultural chemicals *viz.*, pesticides and fertilizers has increased the efficiency of food production in a huge dramatic pattern and has in fact more than fourfold food production in the last century. However, with the advancement of food security, food safety is another issue that needs attention. Indiscriminate use of pesticides leads to many deleterious effects on soil health, plant health, and environmental health consequently affecting the ecological balance. It is associated with huge toxic impacts on human health and the environment. It is quite complicated to determine the exact balance between the advantages as well as the associated harms with pesticide usage because it has been a topic of argument that with the use of agrochemicals mainly, pesticides, on a broad surface, has led to an increment in the quality and quantity of horticultural produce (fruits and vegetables) and consequently has improvised public health, in spite of the potential adverse health effects (Ames, 1983) [26].

The term "pesticide" is an amalgam phrase that in itself 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. From an agriculture perspective, the term pesticide generally includes herbicides, insecticides, fungicides, algaecides, nematocides, and rodenticides.

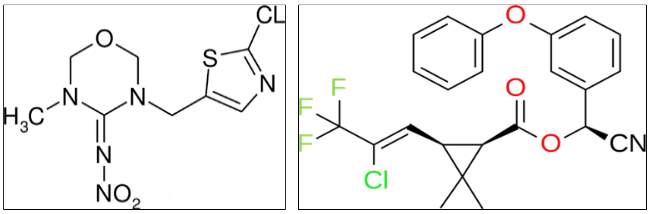
An alternative approach to tackle the wide and complex spectrum of the pest is to formulate a suitable combination of insecticides. These pre-mix combination formulations can be applied as a foliar, seed dressing, and as soil drenching. The mixture produces greater insecticidal action than the sum of the individual action of the components and is said to be synergistic and could be useful for insect control at a premium. One such ready pre-mix formulation is Alika (thiamethoxam + lambda - cyhalothrin) recommended as a foliar in chilli crop to control leaf miner, whitefly, and fruit borer. These insecticides separately or in combination mixture, have been found effective in controlling insect pests of vegetables and thus broadening the spectrum, even for the economy of applications also.

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. 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 a foliar spray in plants as well as to the seeds.

Another dynamic systemic insecticide, Lambda - cyhalothrin [a-cyano-3-phenoxybenzyl-3-(2- chloro-3, 3, 3-trifluoroprop-1-enyl)-2, 2-dimethyl cyclopropanecarboxylate]. It is one of the well- known synthetic pyrethroids with a molar mass of 449.85 gm/mol. It is a non-systemic insecticide with contact and stomach action as well as repellent properties. It is soluble in xylene, ethyl acetate whereas in water its solubility is 0.005 mg/L. It gives rapid knockdown activity to control a wide spectrum of insects pests like aphids, thrips, lepidopteron larvae, coleopteran larvae, and adults in cereals, ornamentals, potatoes, vegetables, cotton, and other crops. It provides good control of insect-borne plant viruses and insect pests in public health.

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 shreds of evidence of acute as well as chronic poisoning based upon the extent of exposure to them. In the 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 phytoplanktons. 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. Ultimately it's all running in a cycle reaching us and moving into the environment. Nature and solubility of pesticides, microbial activity, soil temperature, photodegradation, and rainfall are some of the factors that affect the pollution of water by pesticides. Other than this there are many other factors included. So all these critical issues related to pesticide accumulation in water need to be thought about and proper actions are needed to be taken on. Hence, it becomes mandatory to assess the impact of the use of these from the residues point of view for the safety of the consumers as well as its persistence in soil from the environment safety point of view. Keeping in mind all the ill effects, the present study was designed with the aim to assess the effect of photo-degradation of ready pre-mix formulation of Thiamethoxam+ lambda - cyhalothrin insecticides in irrigation Canal Water under Laboratory Conditions.



Lambda - cyhalothrin Thiamethoxam

Fig 1: Structure of Thiomethoxam+ lambda - cyhalothrin insecticides

Material and Methods

Thiamethoxam, lambda - cyhalothrin samples, glassware, and solvents: Ready-mix formulation of Thiamethoxam + lambda - cyhalothrin (Alika) was purchased from the local market of Hisar, Haryana. A 100 ppm standard stock solution was prepared in acetone 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

Pesticide residue analysis determines not only the parent compounds but also their metabolites and degradation products. As many investigations have confirmed, determining pesticide residues in the range below ng mL^{-1} is difficult and extremely complex because of the need to isolate, accurately identify, and measure such minute quantities in large amounts of extraneous material. Gas chromatography is the most widely adopted technique in pesticide residue analysis. Pesticides that are amenable to direct analysis by means of GC should preferably be determined by means of this method because it separates well, is fast, and has available many selective and sensitive detectors. GC-MS/MS Shimadzu Model GCMSTQ-8040, equipped with split/Splitless injection port and autosampler (Shimadzu AOC 20S) coupled with a 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 °C and 250 °C respectively. All other necessary parameters of the instrument are provided in Table number. 1.

GC MS/MS Parameters

In parameters of GCMSMS helium was used as carrier gas with a flow rate of 1.46 ml min^{-1} through the column and [a] total flow rate of 21 ml min^{-1}. The instrument was run in the split less mode with auto-injection. Retention time through the column was observed to be 13.7 and 20.4 minutes. Limit of Detection and Limit of Quantification was observed to be 0.01 µg/kg and 0.0005 µg/kg. All the parameters discussed above are given in table 1 below.

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 (Rt)	13.7
	20.4
Injection mode	Autoinjector Split less

Laboratory experiment/ trials

The laboratory experiments were carried out from July to November 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 the ready-mix formulation of Thiamethoxam+ lambda - cyhalothrin (Alika) at the rate of 0.5 µg ml^{-1} (SD) and 1µg mL^{-1} (DD). The control sample was left as such. All the bottles along with control were kept open where regular exposure to sunlight was available. Sampling for estimation of residues was performed on 0 (I h), 3, 5, 10, 20, 30, 45, 60, and 90 days after treatment. The Physico-chemical characteristics (i.e, electric conductivity. pH, etc) of canal water are provided in Table. 2.

Table 2: Physico-chemical characteristics of canal water

EC 10x6 (µ sm-I)	242
HCO3 (mel^{-I})	0.45
Ca+2 (mel-I)	1.13
Mg+2(mel-I)	2.1
pH	7.3

Extraction and clean-up

For extraction and clean-up, the method of liquid-liquid partitioning was followed with some modifications. Liquid-liquid extraction/ partitioning (LLE) is also known as solvent extraction and partitioning. It is a method used to separate metal complexes or compounds on the basis of their relative solubilities in two different immiscible liquids i.e. water and an organic solvent. As we know that water is polar and organic solvent is non-polar. There is a net transfer of one or more species from one liquid into another liquid phase, generally from aqueous to organic. This the mainly the chemical potential which is responsible for the transfer i.e. once the transfer is complete, the overall system of chemical components that make up the solutes and the solvents are in a more stable configuration (lower free energy). The solvent enriched in solute(s) is called extract and the feed solution depleted in solute(s) is called the raffinate. This type of process is commonly performed after a chemical reaction as part of the work-up, often including an acidic workup. 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 Na2SO4. Extract in the conical flask was then concentrated on a Rotary Evaporator till near dryness. The final volume of 3 mL was prepared with n-hexane for performing GC-MS/MS analysis.

Calculations for the determination of residues in test samples

$$\text{Residues}(\mu g/g) = \frac{SA_{inj}}{ASA} \times \frac{As}{V_{Sinj}(\mu l)} \times \frac{V_f(ml)}{V_i(ml)} \times \frac{V_{inc}}{W(g)} \times \frac{100}{\%R}$$

$$\text{Per cent Mean Recovery} = \frac{\text{Amount recovered}}{\text{Amount added}} \text{ X } 100$$

Where, SAinj	=	Standard amount injected
ASA	=	Peak area of sample
Vs inj	=	Volume of sample injected
Vf	=	Final volume of sample extract
Vinc	=	Final extract volume for GC
Vi	=	Sample extract aliquot processed
W	=	Analytical sample weight
% R	=	Per cent Recovery

The calculation for regression equations, residues half-life, and rate constants

Half-life is the period of time it takes for one-half of the amount of pesticide in the soil to degrade. Each half-life that passes reduces the amount of pesticide present in the soil by one-half, i.e. 1 to 1/2 to 1/4 to 1/8 to 1/16, etc. Half-life can vary due to soil microbial populations, soil moisture, soil temperature, and other factors. These numbers represent a typical value from the scientific literature. The half-life of residues was calculated by obtaining a linear regression equation between plots of log [residues (µg g^{-1}) x 10^3] and days after application. The log [residues (µg g^{-1}) x 10^3] were spotted on the y-axis and days after application on the x-axis. The least square method was used to find out slope (b) of x and y-axis (Regupathy and Dhamu, 1990).

$$t_{1/2} = \frac{e}{b} = \frac{0.301}{b} \quad [e = \log 2 = 0.301)$$

$$b = \frac{SP_{xy}}{SS_x}$$

$$SP_{xy} = \frac{\Sigma X Y - (\Sigma X)(\Sigma Y)}{n}$$

$$SS_x = \frac{\Sigma X^2 - (\Sigma X)^2}{n}$$

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 @ 0.1, 0.5, 0.01 ppm. The reported results were the 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 percent recovery values of Thiamethoxam+ lambda cyhalothrin insecticide from water with liquid-liquid partitioning were very satisfactory as all the values were above 80 per cent. The respective recoveries ranged from 81.11-88.91and 81.78-89.39 per cent for Thiamethoxam+ lambda - cyhalothrin respectively.

Table 3: Per cent recovery of Thiamethoxam+ lambda cyhalothrin insecticide from water using Liquid-Liquid Partitioning

Fortification Levels (µg g-1)	Replicates	Thiamethoxam		lambda cyhalothrin	
		Recovery (%)	Average* Recovery (%)± SD	Recovery (%)	Average* Recovery (%)± SD
0.1	R1	90.01	88.91±0.82	89.98	89.39±0.73
	R2	88.72		89.85	
	R3	88.02		88.35	
0.05	R1	86.77	85.75±0.93	85.96	84.85±0.91
	R2	84.52		84.88	
	R3	85.98		83.72	
0.01	R1	80.01	81.11±0.83	82.85	81.78±0.76
	R2	81.32		81.06	
	R3	82.02		81.45	

*Average of three replicates

2. Residues in water

Table 4 and Figure 2 below presents the data showing the dissipation pattern of thiamethoxam residues in the water system at single and double doses. It is clearly, examined that the initial average concentration was 0.494 and 0.754 at single and double doses respectively. Residues dissipated up to 60 days at single dose with average values of 0.494, 0.399, 0.342, 0.252, 0.205, 0.119, 0.072 and 0.043, while for double dose the residues persisted up to 60 days after treatment with 0.754, 0.595, 0.476, 0.417, 0.352, 0.272, 0.107 and 0.063 average values. The per cent dissipations ranged as 19.23, 30.76, 48.98, 58.50, 75.91, 85.42, 91.29 at single dose while for double dose 21.51, 37.61, 45.60, 54.39, 65.23, 87.55 and 93.50 per cent dissipation was observed.

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

Days after treatment	Thiamethoxam residues(mgkg^{-1})			
	T1(0.5 µg/ml)		T2(1.0 µg/ml)	
	Average residues *±SD	% Dissipation	Average residues *±SD	% Dissipation
0	0.494 ±0.026	-	0.754 ±0.103	----
3	0.399 ±0.031	19.23	0.595 ±0.066	21.51
5	0.342 ±0.027	30.76	0.476 ±0.053	37.61
10	0.252 ±0.077	48.98	0.417 ±0.012	45.60
20	0.205 ±0.044	58.50	0.352 ±0.065	54.39
30	0.119 ±0.077	75.91	0.272 ±0.013	65.23
45	0.072 ±0.033	85.42	0.107 ±0.010	87.55
60	0.043 ±0.020	91.29	0.063 ±0.029	93.50
90	BDL	-	BDL	
Correlation Coefficient R^2 = 0.988 Regression Equation y= -0.017x + 2.635 t l/2 = 17.70 days			Correlation Coefficient R^2 = 0.973 Regression Equation y= -0.016x + 2.835 t l/2 = 18.81days	

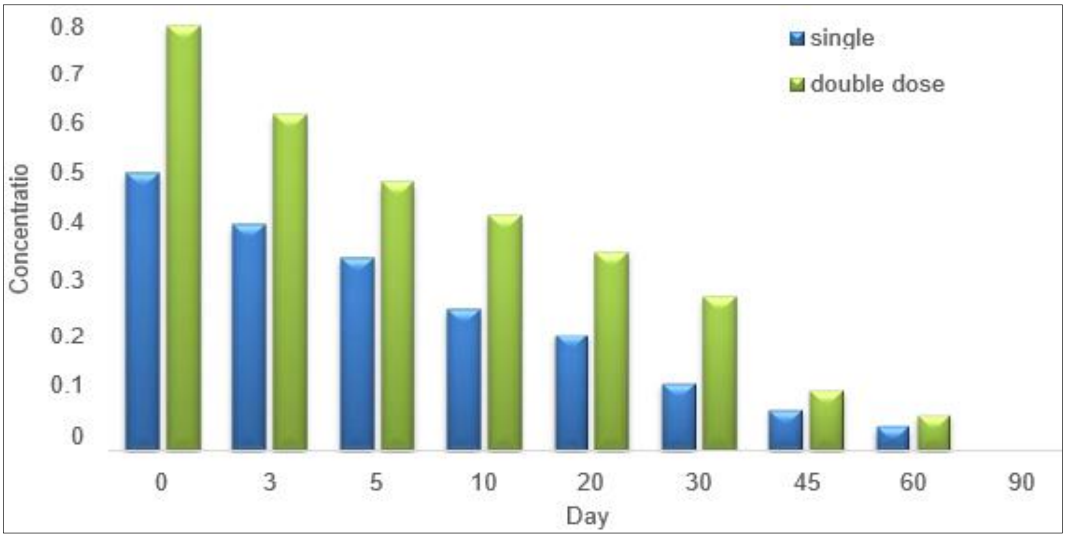


Fig 2: Bar graphs of residues of Thiamethoxam+ lambda - cyhalothrin

Data relating to the dissipation pattern of lambda - cyhalothrin residues in the water system at respective single and double doses is presented in Table 5 and Figure 3. It is clearly, reported that the initial average concentration was 0.265 and 0.332 at single and double doses respectively. Residues persisted up to 30 days at single dose with average values of 0.265, 0.225, 0.156, 0.147, 0.062 and 0.024 while for double dose the residues persisted up to 30 days after treatment with, 0.332, 0.298, 0.216, 0.170, 0.077 and 0.050 average values. The per cent dissipations ranged as 15.09, 41.05, 44.37, 76.56, and 90.75 at single dose while for double dose 10.34, 34.94, 48.8, 76.81, 42.84, and 84.91 per cent dissipation was observed.

Table 5: Persistence of residues of lambda - cyhalothrin (mgkg-1) insecticide in the irrigation water system at single and double dose

Days after treatment	Lambda cyhalothrin (mgkg^{-1})			
	T1(0.5 µg/ml)		T2(1.0 µg/ml)	
	Average residues *±SD	% Dissipation	Average residues *±SD	% Dissipation
0	0.265 ±0.062	-	0.332 ±0.050	
3	0.225 ±0.045	15.09	0.298 ±0.044	10.24
5	0.156 ±0.061	41.05	0.216 ±0.087	34.94
10	0.147 ±0.071	44.37	0.17 ±0.035	48.8
20	0.062 ±0.029	76.56	0.077 ±0.022	76.81
30	0.024 ±0.016	90.75	0.050 ±0.002	84.91
45	BDL		BDL	
60	-		-	
90	-		-	
Correlation Coefficient R^2 = 0.983 Regression Equation y = -0.033x +2.435 t l/2 = 9.12 days			Correlation Coefficient R^2 = 0.984 Regression Equation y = -0.028x+2.513 t l/2 = 10.75days	

The results presented were aligned with those of Dhanker *et al*. (2021), who performed a study on degradation of Chlorantraniliprole + Thiamethoxam in water using liquid-liquid partitioning, the residues were dissipated more than 80% up to 30 (0.024) and 45 (0.06) days in SD and DD, respectively for Chlorantraniliprole and the dissipation rate exceeds 80% for thiamethoxam on 45 (0.048) and 60 (0.073) for SD and DD, respectively. The same experiment was performed by Reena *et al.,* (2008) on the degradation of propiconazole in the water system. All the recoveries were reported to be above 90 per cent. 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.

Conclusions

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

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