

## **The Persistence of Chlorpyrifos and Alphamethrin Insecticides on Cotton Foliage**

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**Abstract.** The persistence of chlorpyrifos and alphamethrin insecticides alone or mixed with chelating fertilizer was studied on/in cotton foliage during the period of pest control on cotton crop under the Egyptian environmental conditions. Chlorpyrifos (48% E.C.) and alphamethrin (25% S.C.) were applied to mature cotton plants at the rate of one and 100 ml per acre respectively. The cotton leaves were sampled for residue analysis at one hour, 1, 3, 7, and 21 days after treatments. GLC methods of analyses were employed for residue determinations.

The data indicated that the residual half life of chlorpyrifos is less than one day and it is 7 days for alphamethrin insecticide. This showed that alphamethrin was more stable than chlorpyrifos under the experimental conditions. The addition of chelating fertilizer slightly decreased the deposits of chlorpyrifos and alphamethrin on cotton foliage in the first 14 and 21 days respectively during the experimental period.

### **Introduction**

Chlorpyrifos (0.0-diethyl 0-3, 5, 6-trichloro-2-pyridyl phosphrothioate) (Dursban) and alphamethrin (IR cis) 5 and (IS cis) R enantiomer isomer pair of (alpha-cyano-3-phenoxybenzyl-3-(2,2-dichlorovinyl)- 2,2-dimethylcyclopropene carboxylate) (Fas-tac) are highly active and cost effective insecticides which control a wide range of pests on crops of economic importance.

A variety of environmental factors, chemical structure and concentration determine the residual life and behaviour of the pesticide chemical in the field [1-6].

Primarily because of economic reasons it is becoming a common practice to apply fertilizer foliarly to crops through pivot system of irrigation in some parts of the world. However, studies on the application of fertilizer along with pesticides to the crops has been given little attention and it was, therefore, thought of value to investigate the stability of chlorpyrifos and alphamethrin insecticides alone as well as

mixed with chelating fertilizer on/in cotton foliage during the period of pest control on cotton crop under the Egyptian summer environmental conditions.

### Materials and Methods

The cotton plants, variety Giza 65, were grown at Bahtim Experimental Station, Qalubia Governorate, Egypt during the summer season of 1984. Mature cotton plants (about 130 days old and 120-130 cm high) were sprayed on July 15, 1984, using chlorpyrifos 48% E.C. and alphamethrin 25% S.C. at the rate of one l (480g active ingredient) and 100 ml (25g a.i.) diluted to 400 l water per acre respectively. Chelating fertilizer of Fe, Mn, and Zn (1: 1.2:1.2) at 340g/acre was mixed with each pesticide chemical at the same rate, diluted with water and applied on the cotton plants in other treatments. A Knapsack sprayer was used in the application of the insecticides. The area under investigation (420m<sup>2</sup>) was divided into 15 equal plots, and each treatment was randomly replicated three times. Three untreated plots were left as control. The cotton leaves were sampled at one hour, 1, 3, 7, 14 and 21 days post treatment for residue determination.

#### Sample preparation

The cotton leaf sample (50g) was well macerated with anhydrous sodium sulphate in a waring blender. 200 ml of benzene and ethyl acetate were used to extract chlorpyrifos and alphamethrin residues respectively. 50 ml of sample extract was filtered through clean bed of cotton and anhydrous sodium sulphate and concentrated to 3-5 ml using rotary evaporator and evaporation was completed to dryness at 40°C with the aid of a gentle stream of nitrogen in a well ventilated hood.

Cleaning up for chlorpyrifos was conducted according to Braun [7] by introducing concentrated benzene extract to 10g activated silica gel column topped with 1 cm anhydrous sodium sulphate, prewashed with 50 ml benzene using small amounts of benzene to effect quantitative transfer. Inside of column was rinsed with additional 5 ml benzene and all eluate collected was discarded to this point and chlorpyrifos was eluted with 50 ml benzene in clean receiver. The eluate was evaporated to dryness with rotary evaporator.

Alphamethrin sample extractions were cleaned up through glass column (15 mm i.d. × 400 mm length with teflon stopcock) containing glass wool plug and 10 g activated florisil topped with 1 cm anhydrous sodium sulphate. The column was washed with 50 ml hexane: dichloromethane (80 : 20). The concentrated sample extract was dissolved in 10 ml hexane/dichloromethane and transferred onto the column and the container was washed twice with 10 ml hexane/dichloromethane and added to column. 250 ml hexane/dichloromethane eluate was collected after discarding the first 50 ml. The eluate was evaporated to dryness using rotary evaporator. 10 ml of acetone was added to alphamethrin residues and concentrated to dryness. Acetone

washing process was repeated two times to remove any traces of dichloromethane and evaporated to dryness.

Residues of chlorpyrifos and alphamethrin were transferred to calibrated flasks and diluted to suitable volume with nanograde benzene and ethyl acetate respectively for GLC analysis.

#### **Gas chromatographic analysis**

Analysis of chlorpyrifos was conducted on a pye unicum 104 gas chromatograph equipped with a flame photometric detector (FPD), Tracor, fitted with a 526 nm filter (selective for phosphorus). The operating conditions were:

Column: A 1.5 m × 4 mm i.d. pyrex glass packed with 4% SE-30 + 6% OV-210 on gas chrom. Q (80/100 mesh).  
Temperature: Injector and column 200°C, detector 210°C.  
Gas flows (ml/min): Hydrogen 100, oxygen 15, air 60 and nitrogen 120.

The retention time ( $R_t$ ) of chlorpyrifos under these conditions was 2.67 min and the average rate of recovery was 87.91%.

Analysis of alphamethrin was accomplished on a pye unicum 104 gas chromatograph equipped with Ni<sup>63</sup> electron capture detector (ECD) under the following operating conditions:

Column: A 1.5 m × 4 mm i.d. pyrex glass packed with 3% OV-101 on gas chrom. Q (100/120 mesh)  
Temperature: Injector and column 250°C, detector 260°C.  
Carrier gas flows: 120 ml nitrogen/min.

The retention time ( $R_t$ ) of alphamethrin under these conditions was 2 min and the average rate of recovery was 93.75%.

The data obtained were corrected according to average rates of recovery which were estimated by adding known amounts of each authentic compound to untreated leaves of cotton plants and subjected to the same technique. Each residue figure represents an average of three samples.

### **Results and Discussion**

The data in Table 1 show the chlorpyrifos and alphamethrin residues alone or mixed with fertilizer on/in cotton leaves at different time intervals after treatments. The residues revealed that the amounts of deposits depend on the rate of application.

**Table 1.** Chlorpyrifos and alphasmethrin residues on cotton foliage (Bahtim Experimental Station, Kalubia Governorate: Egypt, July 1984)-

Period after application	Residues in PPM*			
	Chlorpyrifos	Chlorpyrifos + Fertilizer	Alphasmethrin	Alphasmethrin + Fertilizer
One hour (Initial)	121.19	122.88	10.17	9.79
24 hours	32.26	29.92	8.04	7.47
3 days	23.05	13.55	6.69	5.69
7 days	7.14	4.14	5.46	4.25
14 days	2.90	2.04	1.84	1.72
21 days	0.14	0.61	0.25	0.16

\* Each residue figure represents an average of three replicates.

In case of chlorpyrifos, the initial amounts alone or mixed with fertilizer one hour after treatment under the normal field conditions were almost the same (121.19 and 120.88 ppm respectively). These values dropped during the first 24 hr. to 32.26 and 29.92 ppm respectively. Following that period they decreased to 23.05 and 13.55 ppm respectively 3 days after treatment. A gradual decrease until 0.14 and 0.61 ppm was obtained 21 days after treatment.

The initial deposits of alphasmethrin alone and mixed with fertilizer one hour after application were 10.16 and 9.79 ppm respectively. These values decreased to 8.04 and 7.47 ppm 24 hr. after treatment. Following the 24 hr. period the alphasmethrin residues on/in cotton leaves declined gradually until 0.25 and 0.16 ppm respectively were detected 21 days after treatment.

Data depicted in Fig. 1 show the rate of persistence of chlorpyrifos and alphasmethrin insecticides on/in cotton foliage at different intervals after application. The rate of persistence of chlorpyrifos alone and mixed with fertilizer was 26.62 and 24.35% of the initial deposits 24 hr. after treatment respectively. This demonstrates that the residue half life of chlorpyrifos was less than one day. The rates of persistence of alphasmethrin alone and mixed with fertilizer were 53.74 and 43.41% respectively 7 days after application revealing that the half life of alphasmethrin was about 7 days under normal field conditions. However, 18.11 and 17.47% of the initial deposits of alphasmethrin and 2.39 and 1.66 % of chlorpyrifos alone and mixed with fertilizer respectively 14 days after application indicate that alphasmethrin could be considered a persistent insecticide with a long residual effect when compared with chlorpyrifos insecticide. The results agreed with those obtained by Dickinson [8], Abdel-Razik, *et al.* [2], Berg [6] and hegazi, *et al.* [4] who studied the photodecomposition of some synthetic pyrethroids and OP compounds.

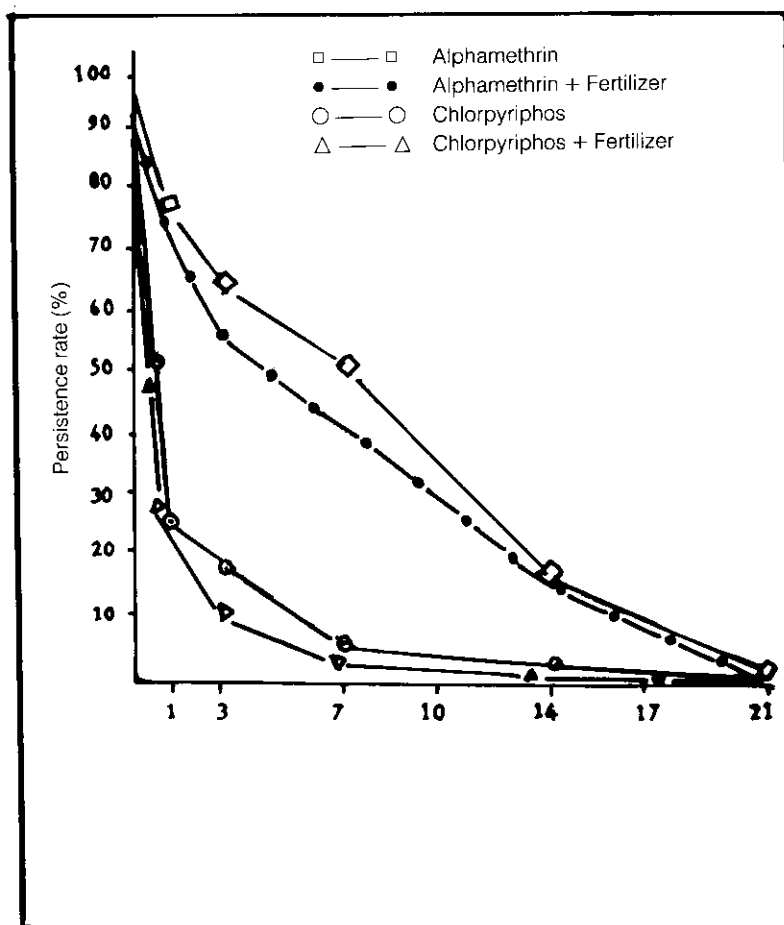


Fig. 1. Percentage rate of persistence of chlorpyrifos and alphamethrin insecticides on cotton leaves.

The data clearly show that mixing of fertilizer with chlorpyrifos and alphamethrin before field application had only a slight effect on the rate of persistence of both insecticides on/in cotton foliage. It shows that chlorpyrifos and alphamethrin deposits decreased slightly in the presence of fertilizer which might at least be attributed in part to the enhancement of plant growth by fertilizer treatments which is reasonable in view of White-Stevens. [9, p. 558]

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## بقايا مبيدات الكلوربيريفوس والألفامثرين على أوراق القطن

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ملخص البحث. أجريت الدراسة على بقاء مبيد الكلوربيريفوس والألفامثرين كل بمفرده أو مخلوطاً مع مخصب ورقي مغلي خلال فترة مساومة آفات القطن تحت ظروف البيئة المصرية. أجري الرش بالكلوربيريفوس ٤٨٪ مركز قابل للاستحلاب والألفامثرين ٢٥٪ مركز قابل للذوبان بمعدل لتر و١٠٠ مليلتر لكل إيكتر على التوالي وأخذت عينات أوراق القطن عشوائياً لتقدير متبقيات المبيدات بعد ساعة واحدة ثم ١، ٣، ٦، ١٤، ٢١ يوماً بعد المعاملات واستخدم الكروماتوجرافي الغازي السائل في التقدير.

اتضح من النتائج أن فترات نصف العمر كانت أقل من يوم واحد للكلوربيريفوس وحوالي سبعة أيام للألفامثرين مشيرة إلى أن مبيد الألفامثرين كان أكثر ثباتاً من الكلوربيريفوس تحت ظروف التجربة كما لوحظ أن إضافة المخصب الورقي أدى إلى الإنخفاض الضئيل لمتبقي الكلوربيريفوس والألفامثرين خلال ١٤، ٢١ يوماً على التوالي.