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Residues of Chlorpyrifos-methyl on Wheat Grains, and Its Effect on Certain Stored-Grain Insects

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Abstract. Two rates ((5 & 10 ppm a.i.) of chlorpyrifos-methyl were applied to wheat grains, stored in tightly-closed glass jars (each 5 L capacity) under the laboratory conditions for 12 months. Insecticide residues and its insecticidal activities were evaluated at different intervals. The results showed that, the percent losses in chlorpyrifos-methyl after 12 months were 52.81% and 59.11% for the lower and higher rates, respectively, without any insecticidal activity to the tested insects: *Trogoderma granarium* and *Tribolium confusum*. The degradation pattern of the insecticide was triphase with t 0.5 = 34 weeks.

Introduction

Chlorpyrifos-methyl, a broad spectrum insecticide with an acute oral mammalian LD_{50} to rats 1000-3700 mg/kg (b.w.), is being considered as a protectant for grain insects attack. Many investigators have studied the efficacy of organophosphorous insecticides against stored product insects. Chlorpyrifos methy at 3 ppm or more controlled rice weevil, *Sitophilus oryza,* granary weevil, *S. granarius* and maize weevil S. *zeamaiz*. He added that a dose as high as 8 ppm was required to kill *Ca* 90% of the lesser grain borrer, *Rhyzopertha dominica,* 83% for the confused flour beetle, *Tribolium confusum* and 98% of the red flour beetle, *T. castaneum,* 12 months after application [1]. Pirimiphos-methyl applied at 10 and 15 ppm, adequately protected rough rice subjected to heavy infestation pressures by multi species insect population for 12 months [2]. A dose of 3.4 ppm of pirimiphos-methyl was superior to a dose of 11.16 ppm of malathion for control of seed corn insects [3]. The present study was performed to determine the efficacy of two dosages of chlorpyrifos-methyl to protect wheat grains from being attacked by two stored grain insect species and stabilized patterns of the insecticide residues degradation on samples of wheat grains (*Triticum aestivum*) during 12 months storage.

Materials and Methods

Wheat treatment

Chlorpyrifos-methyl, [0,0-dimethyl 0-(3,5,6-trichloro -2-pyridinyl) phosphorothioate] was provided as 50% emulsifiable concentrate (EC). Lots of 2000 gm of wheat grains (*Triticum aestivum*) were placed in 5-liter widemouth glass jars and treated with 5 ppm and/or 10 ppm a.i. chlorpyrifos-methyl as water emulsion. The control and all treatments were replicated three times. The emulsions were prepared immediately before use. Five ml of each concentration were applied to the inside wall of the glass jars above the grains level. Immediately after application of the emulsion, the wheat-grain mixed throughly be tumbling for 15 min. The bioassay test was performed according to the method of Le Patourel and Tayeb [4]. At different intervals, 100 gm samples were placed in 500 ml glass jars. Twenty adult insects of *Tribolium granarium* and *Tribolium confusum* were added to each jar. Mortalities were assessed after 24 days from the -treatment. The percent age mortalities were corrected using Abbott's formula [5]. All experiments were maintained in the laboratory with a temperature of 21 ± 1°C.

Residue analysis

Residue analysis of Chlorpyrifos-methyl deposits on wheat grains were carried out at different intervals (0,3,7,10,14,21 days, 1,2,3,6,7,9 and 12 months) after wheat-grains treatment.

Extraction and clean-up procedure

Twenty grams of finely ground wheat of each sample were extracted by shaking with 80 ml of distilled acetone for 30 min using KS 500 Kjanke and Kunkle Shaker. The extract of each sample was filtered and transferred with an additional 30 ml of acetone to a 250 ml round bottom flask. The extract was concentrated to about 3 ml using vacuum rotary evaporator at 40°C. The concentrated extract was transferred to column chromatography packed with 13 gm florisil (60 - 100 mesh) and topped with 2 cm layer of anhydrous sodium sulphate. The column was washed by 30 ml petroleum ether (40-60)/diethyl ether 1:1. The sample was eluate by petroleum ether/ diethyl ether 1:1. The clute was evaporated to dryness using a rotary evaporator and the residue was dissolved in a suitable volume of n-hexane [6].

Gas chromatography

Quantitative analysis of chlorpyrifos-methyl residues in the samples extract were performed using Shimadzu 16 A gas chromatograph, equipped with an electron capture detector (ECD) and 2 M × 3.4 mm (ID) glass column with 1.5% OV-17 +

1.95% OV-210 on chrom. WHP 80-100 mesh. Operating conditions: temps. (°C). injection port 200, column 190, detector 220, carrier gas flow rate 60 ml nitrogen/ min, injection volume was 1 ul. The retention time (R_t) of chlorpyrifos-methyl under those conditions was 5.4 min. with an average rate of recovery 94.95%.

Results

Table 1 reports the average mortalities of *Trogoderma granarium* and *Tribolium confusum* exposed to the treated wheat. All the adults of *Tribolium granarium* and *Tribolium confusum* were dead one week after treatment with 10 ppm of chlorpyrifos - methyl. On the other hand, wheat treated with 5 ppm caused 70% and 60% kill of the exposed insects respectively. At the end of the 8*th* week the percent mortalities of *T. granarium* and *T. confusum* were very low for both rate of application.

Table 1. Average percentage mortality of adult *Trogoderma granarium* and *Tribolium confusum* exposed to wheat treated with chlorpyrifos-methyl

Time of wheat treatment (Weeks)	Application rate 5.0 ppm		10.0 ppm	
	T. granarium	*T. confusum*	*T. granarium*	*T. confusum*
1	70	60	100	100
2	60	55	95	85
3	50	50	70	80
4	45	35	60	70
5	30	25	45	60
6	20	15	30	45
7	15	10	15	25
8	5	5	5	10

Residues of chlorpyrifos-methyl

Figure 1 shows the typical chromatogram of the standard material and the sample, respectively. The retention time (R_t) for chlorpyrifos-methyl under the mentioned conditions was 5.4 min. Table 2 and Fig. 2 indicate chlorpyrifos - methyl residues in ppm found during 12 months after wheat treatment. Gas liquid chromatography analysis immediately after treatment showed that 4.77 ppm and 9.45 ppm (a.i) were initially deposited on wheat grains for the two rates of application (5 and 10 ppm), that means that procedure recovery ranged between 95.4% -

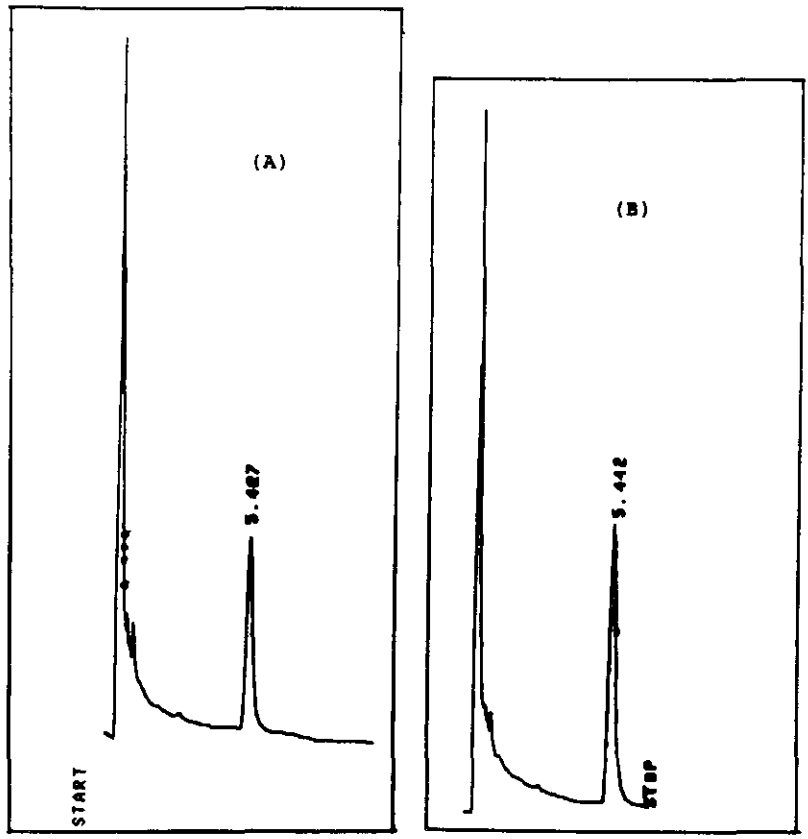

Fig. 1. Chromatograms of the treated wheat extract(A) and the technical material of chlorpyrifos-methyl, 2.5 ng (B).

94.5%. The data show that chlorpyrifos-methyl residues were decreased gradually with increasing storage periods. Twelve months later the amounts first recovered had dropped to 47.17% and 40.42% for the low and high rates of application respectively. The half life time ($t_{0.5}$) of the tested compound was calculated and found to be about 34 weeks.

Discussion

The data in this study showed that chlorpyrifos-methyl had minor effectiveness against two of the stored-product insects; that may be due to the short exposure period (24 hr) to the insecticide tested, because these insects are not grain borrer and

Table 2. Residues of chlorpyrifos-methyl on wheat-grains at different intervals after treatment (mean of three replicates)

Storage Period	Rate of application			
	4.77 ppm		9.55 ppm	
	Residue det. ppm	% Degradation	Res. det. ppm	% Degra.
Days				
3	4.25	10.90	8.89	4.97
7	3.89	18.45	7.89	16.51
10	3.48	27.04	7.79	17.57
14	3.46	27.46	7.50	20.63
21	3.43	28.09	6.96	26.35
Months				
1	3.41	28.51	6.84	27.62
2	3.37	29.35	6.56	30.58
3	3.28	31.24	6.48	31.43
6	3.14	34.17	6.26	33.76
7	2.96	37.95	5.34	43.49
9	2.36	50.52	4.11	56.51
12	2.25	52.83	3.86	59.15

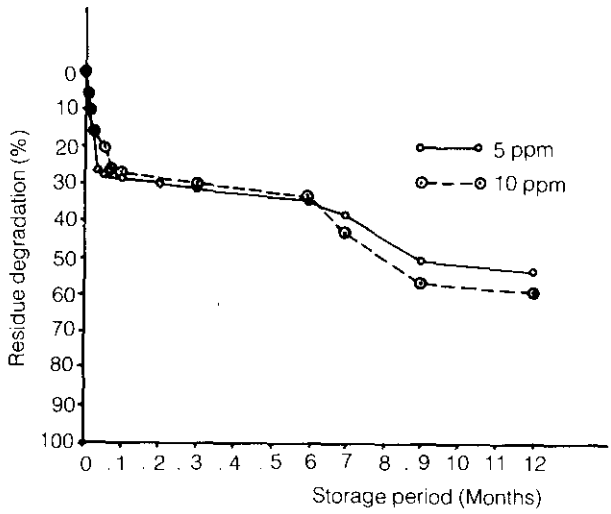

Fig. 2. Percent residue degradation of chlorpyrifos-methyl in treated wheat at different intervals.

they do not get in contact with a large dose of insecticide. Accordingly slight effect was noticed by Samson *et al.* [7], who studied the effectiveness of chlorpyrifos-methyl at 6 mg a.i./kg wheat and pirimiphos-methyl at 15 mg a.i./kg wheat respectively, against *S. oryaze*. They found that these rates gave protection for 1.5 and 6 months, respectively, whereas Cogburn *et al.* [8] found that these rates gave complete protection for 12 months. In the present study 10 ppm gave complete protection for 2 weeks only. La Hue [1], studied the percent degradation of chlorpyrifos-methyl on hard winter wheat using gas liquid chromatography. He reported that degradation percentages of 100 ppm of the insecticide were 15,17,19,22,31,35,45,57 and 72% after 7,14,21 days and 1,2,3,6,9,12 months of treatment. The present study coincides with that data, since the percent degradation were 16.5, 20.6, 26.3, 27.6, 30.6, 31.4, 33.8, 56.5 and 59.15% for the same intervals respectively.

Chlorpyrifos-methyl and many other organophosphates had been evaluated as protectants against stored product grain insects for many years. However, little information has been delivered to the consumer for these hazardous chemicals by manufacturer companies. Therefore, we need many investigations to determine the side effects of these compounds on man and his environment.

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متبقيات المبيد الحشري، كلوربيريفوس ـ ميثايل على حبوب القمح وتأثيرها على بعض حشرات الحبوب المخزونة

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ملخص البحث. تم تطبيق الكلوربيريفوس ـ ميثايل على حبوب القمح بمعدلين (٥، ١٠ أجزاء في المليون مادة فعالة)، وتم تخزين الحبوب في برطمانات زجاجية تحت الظروف المعملية لمدة ١٢ شهرًا. وقدرت متبقيات المبيد في حبوب القمح، وكذلك كفاءة هذه المتبقيات في مكافحة الحشرة الكاملة لخنفساء الخابرا، وخنفساء الدقيق عند أزمنة مختلفة.

وقد أظهرت النتائج أن النسبة المئوية للفقد في المبيد بعد ١٢ شهرًا هي على الترتيب ٥٢,٨١٪ و ٥٩,١١٪ بالنسبة للمعدل المنخفض والمعدل الأعلى من ا لمبيد. كما أظهرت النتائج أن متبقيات المبيد لم يكن لها أي تأثير إبادي على الحشرات المذكورة وذلك بعد شهرين من بداية معاملة الحبوب بالمبيد. وكان نموذج تحلل المبيد من النوع ثلاثي المظهر، وفترة نصف عمر تقدر بأربعة وثلاثين أسبوعًا.