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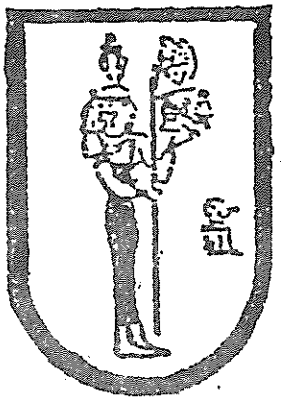

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DISSIPATION RATE OF METHOMYL IN CLOVER FIELDS AND ITS BIORESIDUAL ACTIVITY AGAINST THE EGYPTIAN COTTON LEAFWORM *SPODOPTERA LITTORALIS* (BOISED)

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BY

E.A.Abdalla* and A.Shams,El-Dine**

* Plant Protection Dept. National Research Centre
** Faculty of Agriculture, Moshtohor, Zagazig University.

ABSTRACT

The residual behaviour of methomyl sprayed on clover fields at recommended rate was studied. Samples analysed by High Performance Liquid Chromatography revealed that the initial deposits was 22 ppm, dropped to 12.1 ppm and decreased to 11.4 ppm within the first three days after spraying. A gradual degradation occured, after this initial fast deterioration period, the residues decreased to reach 1.6 ppm and 1.5 ppm after 12 and 16 days of spraying , respectively.

Methomyl also showed high initial toxicity against the second and fourth instars of the cotton leafworm with reasonable persistance; the percent mortality against both instars amounted to 56.9% throughout the experimental period. The results emphasize that methomyl could be one of the most promising insecticides against *S.littoralis* larvae.

Taking into consideration the available tolerance level of methomyl, its daily intake for a given animal and the bioresidual activity against the cotton leafwom, a 12-days interval between spraying and harvest would be quite safe for

INTRODUCTION

The use of oxime carbamate, methomyl [S-methyl N- (methylcarbamoloxy) thioacetimidate] has been extensively increased in the last decade for controlling many lepidopterous larva [Doss et al., 1974; Sheets et al., 1982 and Shaaban et al., 1986].

The clover *Trifolium alexandrinum* is the main forage crop in Egypt, used as winter feedstuff. During the 1991 season, the Egyptian cotton leafworm *Spodptera littoralis* heavly attacked clover plantations and many farmers used methomyl to control it. Some cases of cattle suffering from eating methomyl-treated clover were noticed in Katta village, Giza governorate.

High performance liquid chromatography [HPLC] has been increasingly applied for the separation and direct determination of carbamates[Thean et al., 1977]. HPLC technique avoids several limitations of the use of gas chromatography (GC) for methomyl analysis. Most carbamates are unstable under common GC conditions, they have tendency to break down to the corresponding phenol or they show a conversion to oxime [Lorah and Hemphil, 1974]. The methods based on the derivatization of carbamate to thermally stable products also have limitations that often reduce their sensitivity and versatility [Pease and Kirkland, 1968].

The present work was conducted to study the dissipation rate of methomyl on clover, using high performance liquid chromatography with the ultimate aim of recommending the necessary waiting period between application and harvest and to follow the biological activity of methomyl against *S.littoralis* larvae.

MATERIALS AND METHODS

Clover, grown at Katta village, Gize governorate, was about 20 days old and 25.30 cm high. An area of about 1/4 feddan was divided into 2 equal plots. The first plot was sprayed with methomyl 90% S.P. (Union Carbide Co. Product) at the rate of 300 gm/feddan using 300 liters water. The second one was left as unterated control.

Samples of the whole plant were randomly collected from the treated area one hour after application and then at 0.5, 1.0,3.0, 8.0, 12.0 and 16.0 days after application. They were kept in nylon bags at 20°C until analysis.

Extraction and clean up

For methomyl extraction and cleaning up, the procedure of Thean et al., (1978) was followed. The insecticide was extracted by blending with ethyl acetate. The aqueous extract was cleaned up by partitioning with redistilled hexane. The methomyl was then extracted with chloroform after salting-out. The chloroform was evaporated and the extract was then reduced to a low definite volume and diluted with the mobile phase for HPLC analysis.

Determination:

The HPLC system consisted of a PU 4100 pump equipped with a PU 4110 variable wavelength detector, linked to a P 3120 chromate data system . A wavelength of 240 nm was fixed for detection, which corresponded to the maximum absorbance of methomyl.

A 15 ul volume of the sample was injected into a 10 um MicroPak Rp 18 column (30 cm x 4mm i.d.)

The eluent was acetonitrile: water (15:85 v/v), adjusted to a flow rate of 1 ml min^{-1}. A chromatogram obtained for methomyl is shown in Fig. 1.

Bioresidual activity:

Samples of clover plant were collected at the same periods mentioned before. The residual effect of methomyl was evaluated using a laboratory strain of *S.littoralis*. Ten larvae (2^{nd} or 4^{th} instar) were allowed to feed on treated clover plants in aglass jar. Three replicates were made at each period and an untreated control was included. The mortality count was recorded 24 hrs later and corrected using Abbott's formula. The average percent mortality of the two tested instars was used as the parameter ind cating the bioresidual activity (persisi tance) of methomyl throughout the experimental period.

RESULTS AND DISSUSSION

Residues of methomyl:

Table 1 revealed that a rapid degradation occured shortly after treatment. The initial deposits, 22 ppm, dissipated 12.1 ppm and contiuned to decrease to 11.4 ppm within the first 3 days after spraying. This indicates that the percentage of loss of methomyl after three days was 48.2% / of the initial deposit. El-Sayed et al . (1977) found that about 92% degradation of methomyl occured during the same period on moloukhia leaves (from 123,42 ppm to 9.57 ppm). The initial residues usually vary according to different factors , mainly crop type, pesticide formulation and method of application as well as weather conditions. A slower gradual degradation, however, occured after this initial fast deterioration period. The residues decreased to reach 1.6 ppm and 1.5 ppm after 12 and 16 days after spraying, respectively. Mansour El Gallil (1985) concluded that methomyl was the most persistent compound on clover

Table 1: Residues of methomyl in clover at different days after application.

$$\% \text{ Deg.} = \frac{\text{Initial residues (deposits) - residues in a given day}}{\text{Initial residues}} \times 100$$

	0.0	0.5	1.0	3.0	8.0	12.0	16.0
Residue (ppm)*	22.0	14.6	12.1	11.4	5.2	1.6	1.5
Degradation (%)	0.0	33.6	45.0	48.2	76.4	92.7	93.2

* Corrected according to the percent recovery(78.3%).

Table 2: Bioresidual activity of methomyl sprayed on clover against 2^{nd} and 4^{th} instar S. littoralis larvae.

Instar	% mortality at indicated days after treatment						Avg. % Mortality
	0.0	0.5	1.0	3.0	8.0	12.0	
Second	100	98	92	53.3	25	6.0	---
Fourth	100	100	74	34.0	0	0	---
Average	100	99	83	43.7	12.5	3.0	56.9

among six tested insecticides. Sheets et al., (1982) also indicated that residues of methomyl on Coastal Bermuda grass decline rapidly with time after application, and by days about 7% of the initial deposit remained regardless of the rate applied. In our results, about 23% of the initial deposit of methomyl remained around the same period. The residue of methomyl on clover reached 7% of the initial deposit 12 days after application. Moreover, Braun et al., (1980) found that methomyl residues remaining on head lettuce at 7 days were above the Canadian tolerance level which is 2 mg/Kg. They suggested that a longer waiting period is required to harvest for human consumption.

To recommend a time elapse between application and harvest, data about the tolerance level must be available, which is not available in the case of methomyl on clover. The tolerance level of methomyl on fresh sorghum forage is 1 mg/Kg (CAC, PR, 1990). It may be assumed that the consumption of sorghum forage as summer feedstuff was roughly equal to that of clover in winter. Accordingly, the tolerance level of methomyl on clover will rank between 1 mg/Kg and 2 mg/Kg depending on the daily intake.

In order to calculate time lag required between spraying and harvest we may use an example of the daily intake for an animal (400 kg body weight). It will consume 40 kg clover/day. This corresponds to 64 mg methomyl daily intake. Assuming that the residue level of methomyl on clover after 12 days was 1.6 ppm ; this level is considered safe for animals.However, Hussain et al., (1989) found that administration of methomyl in doses starting from 1 mg/Kg or higher decreased erythrocytic and leucocytic and haemoglobin and packed cell volme percentages in rats.

Bioresidual activity of methomyl:

The results in table 2 showed that methomyl gave complete control in the initial samples against both instars of *S. littoralis* larvae. In spite of the rapid degradation observed in the first hour after spraying (table 1), methomyl kept its toxicity against the two instars and represented 99% and 83% mortality at 0.5 and 1.0 days after application, respectively (table 2). Afterwards, its activity started to decline gradually and the treated plants become free from any effective residues 12 days after spraying . However, the average percent mortality of methomyl throughout the experimental period accounted to 56.9%. Shaaban et al., (1986) found that spraying 150 gm methomyl/fed. on lettuce for controllig *S.littoralis* gave 89.5% intial mortality and 48.03% average mortality throught a 14 days-interval. Increasing the rate to 300 gm /fed gave 96.6 and 58.83 % respectively. They concluded that heads of lettuce were free from any detectable residues at the former rate whereas they were still contaminated by 5.8 ppm methomyl, 14 days after spraying in the last case.

Our results agree with those of Watson et alt., (1982) who found that methomyl applied on cotton plants proved to have good initial kill against *S.littoralis* larvae with relatively long residual action which amounted to 53.3% mortality during 12 days-interval . Although the degradation pattern of methomyl when measured biologically was not identical with that determined chemically, yet it seems that the results in both assessments followed an almost similar trend (Fig. 2).

It could be concluded that the high nitial kill and the suitable persistance of methomyl make it one of the promising insecticides against the Egyptian cotton leafworm. The residues remaining 12 days

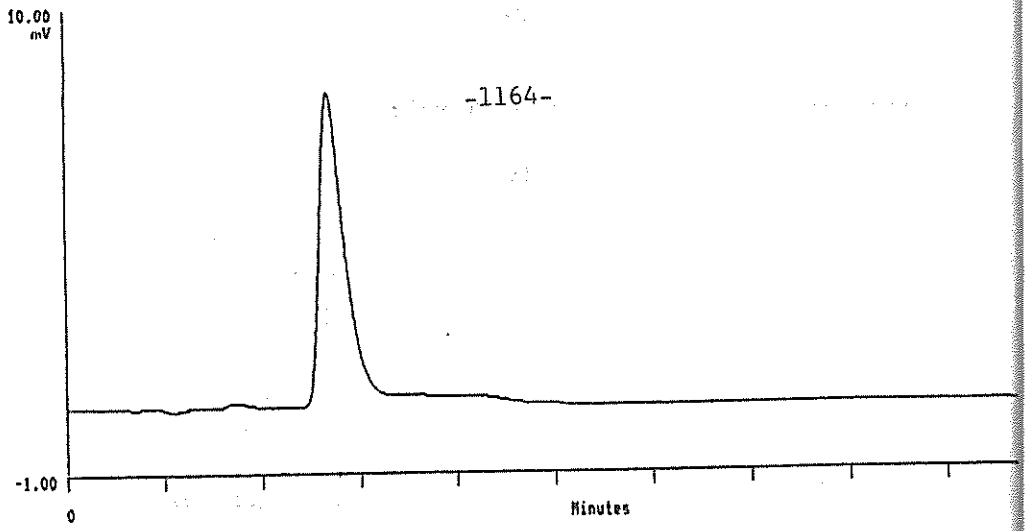
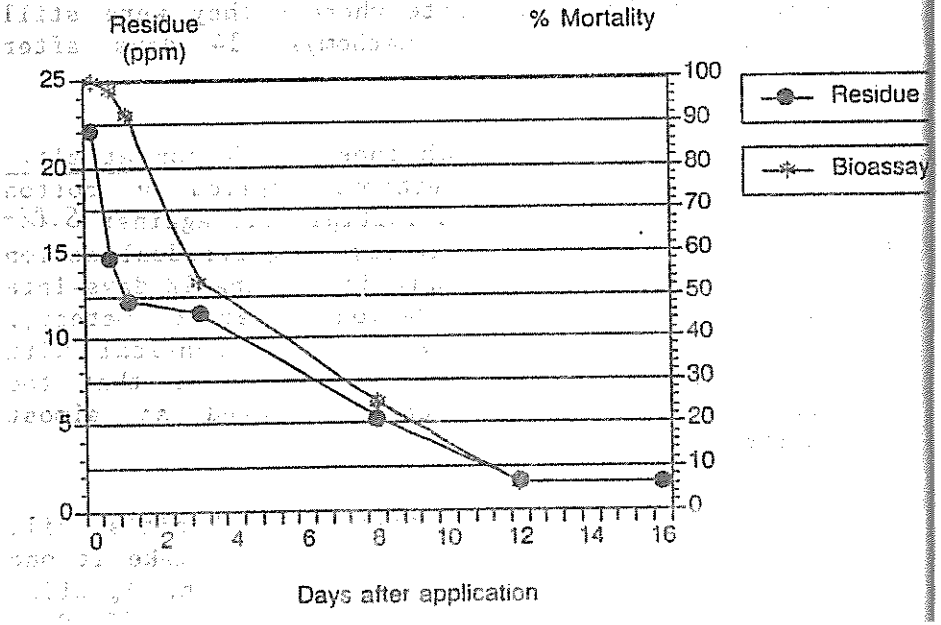


Figure 1: HPLC chromotogram for methomyl extracted from clover plants.



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معدل تدهور ونشاط متبقيات مبيد الميثوميل ضد دودة ورق القطن في حقول البوسيم

السعيد فواز عبد الله* ، علي شمس الدين**

* قسم وقاية النبات - المركز القومي للبحوث

** كلية الزراعة - مشتهر - جامعة الزقازيق

تم دراسة سلوك متبقيات مبيد الميثوميل في حقول البرسيم عند رشه بالتركيز الموصى به. وقد أوضح تحليل العينات أن المتبقيات الآولى قد إنخفضت بمعدل سريع من ٢٢ جزء في المليون إلى ١١.٤ جزء في المليون خلال الثلاثة أيام الأولى بعد الرش. وقد أعقب هذه الفترة فترة أخرى كان معدل إختفاء متبقيات المبيد فيها تدريجياً حتى أصبح ١.٦ ، ١.٥ جزء في المليون بعد ١٢ ، ١٦ يوماً من الرش على التوالي.

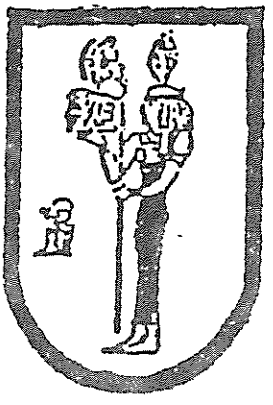
كما أظهر الميثوميل سمية عالية عند تغذية العمرين الثاني والرابع من دودة القطن على أوراق معاملة وإستمرت فعالية واضحة حيث أعطى نسبة موت قدرها ٥٦.٩٪ من اليرقات المعاملة خلال فترة التجربة مما يجعل هذا المبيد في موقع مميز كمبيد فعال ضد هذه الحشرة.

وعند أخذ الحد المسموح لإستهلاك الميثوميل في الإعتبار والكمية التي يمكن أن يستهلكها حيوان المزرعة يومياً منه في غذائه الملوث وكذلك النشاط البيولجي للمبيد حقلياً في مكافحة دودة ورق القطن يمكن القول أن فترة ١٢ يوماً بين الرش وحش البرسيم كافية كفترة آمان قبل إستهلاك البرسيم كعلف أخضر.

المجلة العلمية

لكلية الزراعة

جامعة القاهرة



العدد الرابع

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المجلد (٤٢)

كلية الزراعة - جامعة القاهرة

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