Persistence of Methomyl and Aldicarb as Molluscicides in Different Baits under Laboratory and Field Conditions

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ABSTRACT

Physicochemical properties of five botanical bi-products as carriers were evaluated for preparing methomyl and aldicarb molluscicidal baits (2% a.i). Persistence of these pesticides under tropical, shelf storage and field conditions was investigated. The results indicated that the carriers, except rice bran, have slight acidic pH values. Bulk density values ranged from 0.12 to 0.25 g/cm^3 before compacting and from 0.17 to 0.39 g/cm^3 after compacting. The highest recovery percentages were achieved in case of fine wheat bran (86.4 and 89.6 %) for aldicarb and methomyl, respectively. Decomposition rates of methomyl under tropical storage (54± 2°c) and shelf storage conditions were higher than those of aldicarb baits. Half-life values for aldicarb were greater than 3-folds of those assessed for methomyl at the tested botanical carriers under field conditions. So, aldicarb proved to be more persistent than methomyl baits under storage or /and field conditions.

INTRODUCTION

The land snails are becoming serious pest in Egypt. Annually, damage involving considerable financial losses inflicted on field and horticultural crops (Kassab and Daoud, 1964). Edible baits containing a toxicant are the principle means of molluscicidal chemicals delivery in terrestrial gastropod control programmers (Bailey, 2002). Oxime carbamate pesticides when formulated as baits using botanical carriers were found to be successful for controlling the land snails (Gouch *et al.*, 1968; Hunter and Johnson, 1970; El–Okda, 1976; El-Okda *et al.*, 1989 and El-Shahaat *et al.*, 1992). The bulk of the bait is a foodstuff such wheat bran, which is often used and intended to act as an attractant and a feeding stimulant. Physicochemical properties of these materials vary from one to another. Therefore, the persistence of toxicant active ingredients will be affected by the type of the carrier. The present study was carried out to evaluate the main physico-chemical properties of certain botanical carriers. Testing of persistence is fundamental to commercial product development (Bailey, 2002). So, this work aimed also to study the persistence of prepared methomyl and aldicarb baits under tropical, shelf storage and field conditions.

MATERIALS AND METHODS

1-Preparation of methomyl and aldicarb baits.

Five plant bi-products (botanical materials) were used as carrier for preparing methomyl and aldicarb baits (2% a.i). The selected carriers were wheat bran (fine and coarse fractions obtained using home sieves), rice bran (sersah), rice germah and fine sawdust. The appropriate amount of either methomyl (used as Lannate 90% SP) or aldicarb used as (Temik, 10G) were used for preparing (2% a.i) baits. A mixture of acetone-ethanol-water (1:1:0.5 v/v) containing the pesticide amount was well mixed with the chosen carrier. The obtained baits were treated with methylene blue 0.15% as an attractant color to mollusca, The baits were dried at 40^0C.(EL-Shahaat *et al*; 1995).

2- Physico-chemical properties of carriers.

Bulk densities of botanical carriers were determined before and after compacting (Anonymous, 1967). Equal volumes of the tested botanical carriers 100 cm^3 for each were weight and the volume was estimated before and after compacting for determining the bulk densities as weight per volume. Also, pH values were determined by mixing 20 grams portions of the inert carriers with 100 ml distilled water. After shaking for 1.0 hr., pH values were measured (Watkin and Norton, 1955). Sportive capacity % value was determined by calculating the solvent volume required to saturate 100g of the plant bi-product carrier (Anonymous, 1965).

3- Persistence of methomyl and aldicarb in their baits.

The persistence and decomposition percentages of the tested pesticides in their baits were evaluated under both shelf storage and field conditions for 60 days and 5 days, respectively. Also the decomposition percent was estimaled under tropical conditions (54 ± 2^0C) for 3 days according to specifications reported by Anonymous (1970). Each bait sample was extracted by acetone at the ratio of 1.0 : 25 w/v.The contents had been shaken with 0.1g activated charcoal for one hr. The extraction was by vacuum filteration and the remaining debris was rinsed with additional portions of acetone (about 25ml.). The filtrate was concentrated and cleaned with silica gel-activated charcoal mixture (20:1 w/w) into glass column chromatography. The column was pre-wetted by pet. ether (40-60), while the elution was carried out by successive portions of acetone. The pesticide residues were spectrophotometrically determined according to

Johnson and Stansbury (1966). The efficiency of the method was evaluated using samples fortified by EPA pesticide standard. The half-life value ($t_{1/2}$) was calculated using the following formula:

$t_{1/2} = 0.693/K$

Where $K = \frac{\sum ki}{5}$

$$Ki = \frac{1}{ti} \times 2.3 \ln \frac{a}{mi}$$

mi: the remaining residues (ppm) at *ti* (days).
a: the initial concentration of the pesticide (20, 000 ppm).
K: velocity constant (rate constant of equation in day-1),and
$t_{1/2}$: half-life (in days).

RESULTS AND DISCUSSION

The results in Table 1 indicate that the botanical carriers, except rice bran, have slight acidic pH values ranged between 6.3 and 6.7, versus rice bran which has a slight alkaline pH value (7.4). These results are approximately agreed with those obtained by EL-Okda *et al.* (1982) and EL-Shahaat *et al.* (1995). They found that the botanical carriers have no surface acidic sites. Therefore, these carriers will not affect the persistence of the oxime pesticides in their baits prepared with them. The calculated percent values of solvent sorpitivity indicated that water, acetone and ethanol solvents are acceptable for preparing toxic baits. However, the largest sorpitivity values were related to water (300-455 %), compared to those of acetone (125-240 %) and ethanol (60-240 %). These results show that acetone and ethanol in a mixture are suitable for preparing both methomyl and aldicarb baits. The values of bulk density before compacting ranged from 0.12 to 0.25 g/cm^3 and from 0.17 to 0.39 g/cm^3 after compacting. These results indicated that the volume of the evaluated carriers was decreased by 22.1 to 29.4% as influenced by hand compacting. Acetone and ethanol solvents are suitable for dissolving both methomyl and aldicarb pesticides and can be easily distributed into the pores of the carrier giving a good adherence to the evaluated carriers. Water is not suitable for the preparation of the toxic baits because of the high required quantity of water as indicated by the above mentioned water sorpitivity values (Table 1). So, the high volume of water may ratherly affect the persistence of the pesticides due to the higher moisture contend which also encourage the fungal growth on the carriers, and spoil the prepared baits.

Table 2 shows the efficiency of the extraction method and determination of both methomyl and aldicarb residues in the bait formulations. The recovery percentages are suitable where they ranged between 83.7-89.6% for methomyl and 81.5-86.4% for aldicarb. In this concern the highest recovery percentages were achieved with fine wheat bran fraction (86.4 and 89.6 % for aldicarb and methomyl, respectively). On the other hand, methomyl in its baits decomposed to a range of 51.1-59.7%, while that range was 29.4-40.7% for aldicarb. These results confirmed that aldicarb in its prepared baits was more persistent than methomyl under tropical stability test (54±2 °C for 3 days). Herein it could be also indicated that the efficient and suitable baits must be prepared using ethanol – acetone mixture with a little volume of water. where as under laboratory conditions, the solvents will be evaporated to give a dried bait under about 54 °C. Nevertheless, the farmers usually prepare the baits using water only to reduce the high cost of organic solvents. Under field conditions, the prepared bait must be and fresh prepared daily to avoid the fungal growth on baits and to reduce the degradation of the used pesticide.

Results in Table 3 demonstrate the decomposition percentages of both methomyl and aldicarb under shelf storage at periods of 7, 30, 45 and 60 days. The pesticides decomposition percentages increased from 4.2 up to 47.5 with fine wheat bran bait; 3.6 to 53.0 with coarse wheat bran; 4.7 to 38.2 with rice bran bait; 3.8 to 47.1 with rice germah and 3.1 to 42.6 with fine sawdust bait of methomyl after 7 and 60 days, respectively. In the case of aldicarb baits, the decomposition values were 39.6, 42.7, 30.2, 37.6 and 34.8 after 60 days for the above mentioned carriers respectively.

The first order rate constant and half–life values of the persistence of methomyl and aldicarb in their baits exposed to field conditions in a citrus orchard are presented in Table 4. The persistence of methomyl and aldicarb can be described by the 1^{st} order kinetics. The methomyl residues revealed that the half-life were 3.32, 2.21, 2.50, 1.65 and 3.25 days within those baits prepared using fine wheat bran, coarse wheat bran, rice bran, rice germah and fine wheat sawdust, respectively. Moreover, the obtained results with aldicarb were 11.79, 7.65, 10.71, 5.78 and 13.25 days, respectively. Therefore, it could be concluded that aldicarb is more persistent than methomyl and these results are confirmed by those obtained by El- Okda *et al.* (1983).

Table (1): Some physico-chemical properties of the tested botanical carriers.

Carrier	pH	Solvent sorpativity %			Bulk density(g/cm^3)		Volume decrease %
		Water	Acetone	Ethanol	BC	AC	AC
Fine wheat bran	6.7	300	156	142	0.12	0.29	24.2
Coarse wheat bran	6.6	350	167	172	0.16	0.22	27.8
Rice bran	7.4	420	170	151	0.25	0.39	29.4
Rice germah	6.4	455	125	60	0.17	0.17	22.1
Fine sawdust	6.3	360	240	240	0.24	0.26	26.0

BC: before compacting.

AC: after compacting.

Table (2): Percent recovery and decomposition of methomyl and aldicarb baits stored under tropical conditions (54 ± 2 °C).

Baits	Methomyl		Aldicarb	
	Recovery %	Decomposition %	Recovery %	Decomposition %
Fine wheat bran	89.6±1.5	59.7 ±0.6	86.4±1.0	37.5±0.4
Coarse wheat bran	87.7±1.2	56.2±0.5	84.7±1.2	34.1±0.3
Rice bran	87.5±1.6	62.6±0.7	84.8±1.1	40.7±0.6
Rice germah	85.2±1.6	47.1±1.2	82.4±0.9	25.7±0.7
Fine sawdust	83.7±1.1	51.1±0.7	81.5±1.2	29,4±1.1

Values are means of 5 replicates ± SD

Table (3): Decomposition of methomyl and aldicarb baits under shelf storage.

Baits	Pesticide decomposition %							
	Methomyl				Aldicarb			
	Days of storage							
	7	30	45	60	7	30	45	60
Fine wheat bran	4.2±0.2	24.6±1.1	30.4±0.4	47.5±1.5	2.1±0.2	16.4±1.6	22.6±1.0	39.6±1.7
Coarse wheat bran	3.6±0.5	21.6±0.8	27.5±0.2	53.0±0.6	1.5±0.2	13.5±1.7	19.7±1.5	42.7±2.1
Rice bran	4.7±0.5	28.3±0.6	30.6±0.7	38.2±0.7	2.5±0.3	19.6±1.1	26.1±1.5	30.2±2.5
Rice germah	3.8±0.4	25.7±0.6	31.7±0.6	47.1±0.6	1.9±0.4	17.6±1.2	23.7±1.6	37.6±1.5
Fine sawdust	3.1±0.5	18.8±0.7	24.7±0.4	42.6±0.8	1.2±0.6	10.5±1.5	16.8±1.4	34.8±1.1

Values are means of 5 replicates ± SD

Table (4): First order rate constant(K) and half- life values ($t_{1/2}$)of methomyl and aldicarb prepared as baits with different botanical carriers.

Baits	Methomyl		Aldicarb	
	K (day $^{-1}$)	$t_{1/2}$ (day)	K (day $^{-1}$)	$t_{1/2}$ (day)
Fine wheat bran	2089×10^{-4}	3.32	588×10^{-4}	11.79
Coarse wheat bran	3131×10^{-4}	2.21	906×10^{-4}	7.65
Rice bran	2773×10^{-4}	2.50	647×10^{-4}	10.71
Rice germah	4209×10^{-4}	1.65	1198×10^{-4}	5.78
Fine sawdust	2134×10^{-4}	3.25	523×10^{-4}	13.25

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الملخص العربي

ثبات طعوم الميثوميل والألديكارب كمبيدات للرخويات تحت ظروف المعمل والحقل .

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أجريت عدة تجارب تهدف الى دراسة بعض الخواص الفيزيائية والكيميائية لخمس من المواد النباتية المستخدمة في تجهيز الطعوم السامة في مجال مكافحة رخويات التربة . كا استهدفت الدراسة تقييم ثبات طعوم الميثوميل والالديكارب باستخدام تلك المواد الحاملة وذلك تحت ظروف التخزين الاستوائي وظروف التخزين العادي (فوق الرف)وكذلك الظروف الحقلية وقد أوضحت الدراسة النتائج التالية :–

المواد النباتية الحاملة المختبرة عدا سرسة الارز – لها قيم pH حامضية بدرجة قليلة أما سرسة االأرز فلها قيمة pH قليلة القلوية وبدراسة خاصية القدرة الامتصاصية اتضح أن قيم إمتصاص الاسيتون والايثانول بواسطة المواد الخاضعة للدراسة هي قيم مقبولة لتحضير طعوم جاذبة حيث تتراوح قيم الامتصاص ما بين ١٢٥ إلى ٢٤٠% مع الاسيتون ومن ٦٠إلى ٢٤٠% مع الايثانول. وأوضحت النتائج ان قيم الكثافة الشاملة للمواد الحاملة تتراوح من ٠,١٢– ٠,٢٥ جم / سم٣ بدون تضاغط للحبيبات أما بعد التضاغط فان الكثافات تتراوح من ٠,١٧–٠,٣٩ جم/سم٣. أوضحت الدراسة أن أعلى كفاءة لطريقة الاستخلاص كانت مع الردة الناعمة حيث كانت نسب الاسترجاع ٨٩,٦، ٨٦,٤% مع مبيدي الالديكارب والميثوميل على الترتيب . وصلت نسبة تحطم الالديكارب في الطعوم المجهزة والمختبرة تحت ظروف التخزين الاستوائي إلى مدى يتراوح من ٢٩,٤ إلى ٤٠,٧% بينما وصلت هذه النسبة في حالة الميثوميل إلى مدى ٤٧,١– ٦٢,٦% . نتائج ثبات كل من الميثوميل والالديكارب في الطعوم تحت ظروف التخزين المعملي (التخزين فوق الرف) لفترات حتى ٦٠ يوما أوضحت أن معدل تحطم الميثوميل أعلى منه فى حالة الالديكارب مع جميع المواد الحاملة. كذلك أوضحت النتائج أن جميع فترات نصف العمر لمبيد الالديكارب كانت أكبر من ثلاثة أضعاف مثيلاتها لمبيد الميثوميل مع جميع المواد الحاملة المختبرة مما يدل على أن مبيد الالديكارب أكثر ثباتا من الميثوميل سواء تحت ظروف التخزين المختلفة أو تحت الظروف الحقلية كطعوم سامة لرخويات التربة.