# TOXICITY OF CERTAIN COPPER FUNGICIDES AND OTHER PESTICIDES TO TERRESTRIAL SNAILS

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# **ABSTRACT**

Toxicity of certain copper fungicides to the small garden snail, *Theba pisana* was evaluated fed on sprayed cabbage leaves at the concentrations of 0.5%, 0.25% and 0.125%. According to  $LT_{50}$  values. The obtained  $LT_{50}$  values were 4.67, 5.18 and 8.41 day, with copral; 5.62, 6.39, and 7.54 days for Kocide 2000, 5.47, 5.59 and 9.40 days for Galbin copper, respectively. Besides, molluscicidal efficacy of the copper fungicides, against the small garden snail, *Theba pisana* fed on sprayed lettuce leaves was carried out. The  $LT_{50}$  values expressed in were 2.67 for copper Acrobate (5% Cu, as copper oxychloride), 3.50 for Kocide 2000 (5% Cu, as copper hydroxide) and 2.17 for Galbine copper (5% Cu, as copper oxychloride + benalxyl).

On the other hand, the toxicity of poisoned baits against the brown garden snail, *Eobonia vermiculata* was assessed. *Baits of* methomyl (2% a.i.), cadusafos (2% a.i.), carbendazim (2% a.i.), Copral (5% Cu), Kocide 2000 (5% Cu) and imidichlopride (2% a.i), gave LT<sub>50</sub> values of 1.54, 6.19, 7.00, 4.39, 4.94 and 6.52 days, respectively.

Toxicity of poison baits to the white sand snail, *Helicella vestalis* was assessed by baits of Lannate (methomyl) 2% a.i., Rugby (cadusafos) 2% a.i., Kocide 2000 Copper oxychloride (2% Cu), kemazed (carbendazim)., 2% a.i., and Confidor (imidichlopride) 2% a.i. The obtained LT<sub>50</sub> values were 3.40, 6.48, 10.62, 6.10 and 8.73 days, respectively.

#### INTRODUCTION

Land snails are considered as serious economic pests in the world due to its considerable damage of several types of plants. These attack leaves, flowers, roots, buds, and even the trunk of trees. In Egypt, the land snails are known as a dangerous pests to field crops, vegetables, orchards and ornamental plants especially in the northern coastal areas (El-Okda 1980, Ghamry et,al 1993, El-Deeb et,al 1996 and Eshra 2004). The present study is aimed to evaluate the toxicity of cooper fungicides; Copral 50%, Galben copper 46% WP, Acrobat copper 46% WP, kocide 2000 53.8% DF (copper hydroxide), Kemazed 50% WP (carbendazim), and copper sulfate against. Also certain insecticides; Lannet 90% (methomyl), Rugpy 10% G, (cadusafos), and Confidor 20% SC (imidichlopride) were evaluated against Eobnia vermiculata, Helicella vestalis and Theba pisana land snails under laboratory conditions.

#### **MATERIALS AND METHODS**

#### 1. Snails

The adults of the brown garden snail, Eobania vermiculata (Muller), the small sand snail, Helicella vestalis (Pfeifer) and the small garden snail,

#### El-Shahaat .M.S. et al.

Theba pisana (Muller) were collected from Alexandria and El-Beheira Governorates and fully acclimatized to laboratory conditions prior to the testing and fed on lettuce leaves prior to the experiments.

## 2. pesticides used

#### 2.1. Funficides

Copral 50% WP; copper oxychloride

Galbin copper 46% WP; benalaxyl (Methyl N-Phenyl acetyl-N-2,6 xylyl-DL-alanninate) + copper oxychloride

Acrobat copper 46% WP; dimethomorph (E, Z): 4-[3-4-chlorophenyl]-3-(3,4-dimethoxy phenyl) acrylayl)] morphaline.

kocide (2000) 53.8% DF; Copper hydroxide (Cu(OH)<sub>2</sub>)

Kemazed 50%WP: methylbenzimidazol-2-ylcarbamate

Copper sulfate 43% WP; (CuSO<sub>4</sub>, 5H<sub>2</sub>O)

#### 2.2. insecticides

Lannet 90% SP:(Methomyl); S-methyl N-(methyl carbamoyloxy) thioacetimidate.

Rugpy10% GR: (Cadusafos); S,S-di-Sec-Natyl-O-ethyl Phosphorodithioates. Confidor: (Imidacoloperide); 1-(6-chloro-3- = pyridylmthyl)-N-nitromidazolidin-2-ylideneamine.

## 3. Poison bait preparation:

The toxic baits were prepared using botanical bi-products and the above mentioned commercial formulations of the pesticides. The botanical substances were used as carriers and food attractants. The chosen substances were wheat bran (fine fraction) and fine fraction of sawdust in a mixture of (1:1 w/w). The appropriate amount of each tested pesticide was well mixed with a mixture of acetone: ethanol: water (3:1:0.5 v/v) or water only with the copper fugicides, and mixed with wheat bran + sawdust mixture 1:1 (w/w). The obtained baits were coloured using an aqueous solution of a blue paint substance (0.5%) as colour attractant for gastropods. The prepared baits involved pesticides in their concentrations as follows: Kocide 2000 (5% Cu as copper hydroxide), Acrobate/copper (5% Cu as copper oxychloride), Capral (5% Cu as copper oxychloride), Galben/copper (5% Cu as copper oxychloride), Confidor (2% imidachlopride) and Rugby (2% cadusafos). The methomyl bait (2% a.i) is used as a standard molluscicide.

## 4.Laboratory molluscicidal activity of certain pesticides:

The laboratory tests were carried out in sealed plastic vessels (22 x 15 x 10 cm) with three replicates, each contains 10 adults of the chosen snall species with similar shell size and replicated three times. Four tests were done. The 1<sup>st</sup> one was carried out to evaluate the efficiency of some copper fungicides against *Theba pisana* snall according bioassay feeding technique therefore sprayed cabbage leaves have been offered as discs of approximately 5 cm diameter. The treatments were; Copral, Kocide 2000, and Galben/copper. Each fungicide was sprayed on leaves at three aqueous concentrations; 0.50, 0.25 and 0.125%. The 2<sup>nd</sup> test was carried out using the same technique with lettuce leaves which have been sprayed with Acrobate copper (5% Cu), Kocide 2000 (5% Cu) and Galben copper (5% Cu) and offered to *Theba pisana* snall. The 3<sup>rd</sup> test was excuted with *Eobania* 

vermiculata snail which exposed to baits of cadusafos (2% a.i), carbendazim (2% a.i), Copper oxychloride (5% Cu), copper hydroxide (5% Cu), imidachlopride (2% a.i) and methomyl (2% a.i). The 4<sup>th</sup> test was executed out with *Helicella vestalis* snail using 2% poison baits of methomyl, cadusafos, copper hydroxide, imidachlopride and carbendazim pesticides.

Moreover, in the all prementioned tests, the killed snail individuals were removed daily and the accumulative mortality effects were recorded up to 6 or 7 days post treatment. The mortality percentages were corrected using Abbott's formula (1925) and then exposed to the angular transformation. The lethal time (LT<sub>50</sub>) for 50% mortality was estimated.

#### RESULTS AND DISCUSSIONS

#### 1.Bioassay of the tested fungicides against certain land snails:

The efficiency of certain copper fungicides against the small garden snail, *Theba pisana* (Muller) was evaluated by feeding the snails on sprayed cabbage leaves under laboratory conditions. Results shown in Table (1) indicated that the calculated mortality values (%) as a cumulative effect up to 6 days of treatment, were gradually increased with time.

Table (1): Toxicity of certain copper fungicides against the small garden snail, *Theba pisana* (Muller) fed on sprayed cabbage leaves.

Treatments /			cumulative		
Concentration	0-1	0-2	0-3	0-6	LT 50
	day	days	days	days	days
Copral copper exychloride (0.5%)	10.0 + 0.0	30.0 + 0.0	45.0 + 3.1	60.0 + 0.0	4.67 + 0.50 b*
Copral copper oxychloride (0.25%)	0.0 + 0.0	26.7 + 3.3	36.7 + 3.3	56.7 + 0.3	5.18 + 0.30 b
Copral copper oxychloride (0.125%)	0.0 + 0.0	16.7 + 3.3	26.7 + 3.3	33.3 + 0.4	8.41 + 0.80 a
Kocide 2000 copper hydroxide (0.5%)					
Kocide 2000 copper hydroxide (0.25%)					
Kocide 2000 copper hydroxide (0.125%)	l	!			
Gaibine copper oxychioride + benalaxyi (0.5%)		ļ			
Gaibine copper oxychloride + benalaxyi (0.25%)	0.0 + 0.0	10.0 + 0.0	26.7 + 3.3	5.3 + 3.3	5.59 + 1.40 b
Galbine copper exychloride + benalaxyl (0.125%)	0.0 + 0.0	6.7 + 3.3	10.0 + 0.0	20.0 + 0.0	9.40 + 0.30 a

Values with some letters are not statistically different.

The deduced mortality values were 60.0, 56.7 and 33.3% after 6 days after snails fed on the treated leaves with copper oxychloride fungicide at the concentrations of 0.5%, 0.25% and 0.125%, respectively. The corresponding LT<sub>50</sub> values were 4.67, 5.18 and 8.41 respectively. Mean while % mortality values for copper hydroxide amounted 46.7, 26.7 and 20.0, respectively. These values were corresponded to LT<sub>50</sub> values of 5.62, 6.39

and 7.54 days at its tested concentrations of 0.5%, 0.25% and 0.125%, respectively. The same concentrations of Galbine copper fungicide (0.5, 0.25 and 0.125%) gave % mortality values of 55.0, 53.2 and 20.0 corresponding with the calculated  $LT_{50}$  values of 5.47%, 5.59 and 9.40, respectively.

Molluscicidal effect of the tested copper fungicides against the small garden snail, *Theba pisana* on laboratory treated lettuce leaves is shown in Table (2). The % mortality as accumulative effect indicated that the fungicides could be descendingly arranged as follows: Kocide (2000) or/and Galbine copper (5% Cu) (100.0% mortality) > Copper acrobate, (84.3%). According to the substracted LT<sub>50</sub> values, it is clear that Galbine copper fungicide had the highest effect to kill 50% of the treated snails.

These results exhibit that the Copper fungicides may be useful as molluscicides through spraying application on vegetable plants at the concentration rate of 0.5%. Herein, these tested inorganic compounds appeared to be effective as molluscicides. The efficiency of inorganic copper salts are in agreement with those obtained by many investigators (Lang and Mocleods, 1941; Glendonning, 1952; Winkler and Chi, 1964; Barry, 1969; Van Dinther, 1973 and Shoeb, 1975) and El-Shahaat *et al.* (under publication). El-Wakil and Mesbah (1995) evaluated the low concentrations of Copper sulfate solutions; (0.25, 0.5, 1.0 and 1.5 g/L water on the infestation rate with *Theba pisana* (Mulier) snails for *Vicia faba* L., in the field. During the first 45 days of the experiment, the plants were sprayed after germination every 15 days for three times with each tested concentration. The occurred number of *Theba pisana* snails on the treated plants were monthly counted along five months from January to May.

Table (2): Molluscicidal efficacy of certain copper fungicides against the small garden snail, *Theba pisana* (Muller) fed on treated lettuce leaves.

Fungicides	% Mort				
	0-1day	0-2days	0-3days	0-5days	LT 50(Days)
Acrobate copper; 5% Cu (as copper oxychloride)	25.0 + 0.0	50.0 + 0.0	65.3 + 2.9	84.3 + 3.0	2.67 b
Kocide; 2000 5% Cu (as	~				
copper oxychloride)*	66.7 + 4.4	46.0 + 2.9	96.3 + 0.7	100.0+0.0	3.50 a
Galben copper; 5% Cu (as					
copper oxychloride)	36.0 + 2.1	45.0 + 5.8	70.7 + 5.8	100.0+0.0	2.17 c

\* : Values having the same letters are not statistically different.

It was also obtained that a significant decrease in the numbers of snails among different treatments was achieved. The concentrations of 1.0 and 1.5 g/L exhibited the highest effects in decreasing the percentage number of snails at the end of the experiment (96.56%). The concentration of 1.5 g/L copper sulfate solution gave the highest productivity of plants and decrease in the number of occurring snails. The toxicity and efficacy of copper fungicides may be attributed to the explaination reported by Schiide et al. (2003) who concluded that the foots of the terrestrial gastropods are the sites of copper uptake. The foot is an important penetration routs for highly soluble copper salt, which can be expected to cause some internal damage

and irritant effects. These illustrations are paralleled with that previously reported by Ryder and Boweron (1977). Also, the irrilation effect of copper salts can cause significant dehydrogenation of snails and slugs.

Results in Table (3) indicate the toxicity of prepared poison baits of certain tested pesticides against the white sand snail, *Helicella vestalis*. The a accumulative % mortality values amounted to 100.0, 35.0, 21.3, 42.3 and 15.3 up to 6 days of feeding on the prepared baits of methomyl (Lannate), Cadusafos (Rugby), Carbendazim (Kemazed), Kocide 2000 and Imidachlopride (Confider), respectively. These results corresponded to the LT<sub>50</sub> values of 3.40, 6.48, 10.62, 6.10, and 8.73 days, respectively.

Table (3): Toxicity of tested poison baits to the White Sand snail,

Baits	accumulative corrected mortality % at indicated days + SD*							
	0-1 day	0-2 days	0-3 days	0-4 days	0-5 days	0-6 days	(Days)	
Methomyl (2% a.i)	14.6+ 1.1	36.7+ 1.2	56.6+ 1.1	70.3+ 1.7	90.0+ 1.0	100.0+0.0	3.40 d	
Cadusafos (2% a.i)	2.0 + 1.2	4.7 + 2.7	16.7+ 1.7	23.3+ 1.0	28.7+ 2.1	35.0+ 3.1	6.48 c	
Carbendazim [2% a.i)	0.0	10.0+ 1.5	12.3+ 2.0	14.7+ 3.5	17.3+ 1.2	21.3+ 0.7	10.62 a	
Kocide 2000  2% Cu}	1.7 + 2.5	5.0 + 1.4	12.3+ 2.6	24.3+ 1.1	30.0+ 2.0	42.3+ 2.7	6.10 c	
midachlopride (2% a.i)	0.0	0.0	3.7 + 1.0	6.7 + 0.7	8.3 + 1.0	15.3+ 0.9	8.73 b	

<sup>\*:</sup> Each value is an average of 5 replicates (10 snall each) + standard deviation and the values with the same letters are not significantly different.

From the obtained results it could be noticed that the highest toxicity effect was recorded with for methomyl bait (2% a.i.); followed by the fungicide Kocide 2000 bait (2% Cu); while the remaining pesticides gave less efficacy.

In addition, the results illustrated in Table 4 elucidate the toxicity of the poison baits of six tested pesticides to the brown garden snail, *Eobania verniculata* 

Table (4): Toxicity of poison baits to the brown garden snail, *Eobania* vermiculata (Muller).

	accumula	LT 50 ***			
Baits					
	0-1 day	0-2 days	0-5 days	0-7 days	
Methomyl bait (2% a.i)**	33.1 + 1.7	76.7+1.67	91.6 + 2.2	100.0+0.0	1.54 d
Cadusafos (2% a.i)	10.0 + 1.2	25.0+2.90	40.0 + 2.9	55.0 + 1.7	6.19 b
Carbondazim (2% a.i)	0.0 + 0.0	2.0 + 1.00	23.0 + 2.4	61.3 + 2.4	> 7.00 a
Copral (5% Cu)	20.0 + 2.9	53.3+6.70	63.3 + 1.7	80.0 + 0.0	4.39 c
Kocide 2000 (5% Cu)	10.0 + 1.2	33.3+3.30	53.3 + 3.3	83.3 + 4.4	4.94 c
midachiopride (2%)	5.3 + 0.9	7.0 + 1.20	25.0 + 5.0	64.3 + 2.3	6.52 ხ

<sup>:</sup> Each value is an average of 3 replicates (10 snall each) + standard deviation.

<sup>\*\* :</sup> This baits is taken as a standard treatment.

<sup>\*\*\* :</sup> Lethal time (day) for 50% killing.

The highest a accumulative mortality (%) is recorded to methomyl (100.0%) followed by Kocide 2000 (83.3%) and Copral (80.0%). The remainders gave lower values which are ranged between 55.0 and 64.3 indicating that Cadusafos had the lowest effect (55.0%) after 7 days of exposure. The LT<sub>50</sub> values confirmed that methomyl was the highest efficient treatments (1.54 days) followed by Copral (4.39 days) then Kocide (4.94 days).

From the above mentioned results it could be revealed that the applications of inorganic copper compounds either by foliar sprays or by involving then in poisonous baits were effective against the tested land snails.

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سمية بعض مبيدات الفطريات النحاسية والمبيدات الأخرى ضد القواقع الأرضية محمد سعيد الشحات'، نجده احمد على ، السيد حسن عشره ، حسن على مصباح' وامتياز إبراهيم غنيم "

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تم تقييم سمية بعض المبيدات الفطرية المحتوية عى عنصر النحاس ضد قوقع الحدائق الصغير وذلك عن طريق تغذية القواقع على لوراق الكرنب المعاملة بتركيسزات مختلفة مسن الكويرال (٥,٠،٥٠٠, ١٢٥٠، ١٢٥، ١٢٥، ١٤٥ مين كانت قيم الوقت السلازم لقتسل ٥٥٠ مسن الافسراد المعرضة لهذا المركب هي ٢٠،٤، ١٥،١٥، ١٤٥، يوم على التوالي. كما تسم استخدام مركب الكوسيد ٢٠٠٠ بتركيزات ٥,٠،٥، ١٢٥، ١٢٥، حيث كان الوقت السلازم لقتسل ٥٠٠ سن الأفراد هو ٢٠،٥، ١٣٥، ١٥٥، يوم. أما عند استخدام مركب جالبين النحاس بنفس التركيسزات فقد كانت هذه المدد ٧,٥، ٥، ٥، ٥، ١٩، يوم على التوالي.

- كذلك تم تقييم كفاءة مبيدات النحاس الفطرية المختبرة لاستخدامها كمبيدات قواقسع ضد قوقسع الحديقة الصغير Theba pisana حيث تم تغذية الافراد المختبرة على اوراق خس مرشوشة بتركيزات ثابتة من النحاس (9%) من كل من اكروبات والكوسيد وجالبين النحاس حيث قدرت المدة اللازمة لقتل ٥٠٠ من الافراد المختبرة فكانت ٢,٦٧، ٥,٠٠ ، ٢,١٧ يوم على التوالي.
- بالاضافة الى تقييم سمية بعض الطعوم على قوقع الرمل الابيض H. Vestalis وذلك باستعمال طعوم بتركيزات ٧٣ من مبيدات القواقع التي استعمات وهي مركبات الميثوميل والكادوسافوس والكربندازيم والكوسيد ٢٠٠٠ والايميدكلوبرايد حيث كانت المدة اللازمة لقتل ٥٠٠ من الافراد المتغذية على هذه الطعوم هي ٢٠٤٠، ٢٠٤٠ ، ١٠٦٠، ١٠،١٠ ومن التوالي.
- كما تم تقييم سمية بعض الطّعوم السامة ضد قوقع الحدائق البني وذلك باستعمال طعوم ٢% (مادة فعالة ) من كلاً من الميثوميل وكادوسافوس ، كاربندازيم والايميدكلويرايد ، واستعمال طعوم ٥٠ من كلاً من الكويرال والكوسيد فكان الوقت اللازم لقتل ٥٠٠ من الافراد المعرضة للطعم هو ١,٥٤ ، ١,١٩ ، ٢,١٠ ، ٢,١٩ و ٢,٠٢ يوم على الترالي.