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Pirimiphos-methyl: Gradient of Effective Doses on Hard Winter Wheat Against Attack of Four Species of Adult Insects[1,2]

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ABSTRACT

Pirimiphos-methyl was applied to cleaned hard winter wheat as a water emulsion at gradient doses from 1–10 ppm AI. Then the relative effectiveness of residues in samples withdrawn at intervals during a 12-mo storage period was determined against adults of 4 common species of stored-grain insects. The order of tolerance was: confused flour beetles, *Tribolium confusum* Jacquelin duVal, > lesser grain borers, *Rhyzopertha dominica* (F.), > red flour beetles, *Tribolium castaneum* (Herbst), > rice weevils, *Sitophilus oryzae* (L.).

Pirimiphos-methyl, a broad spectrum insecticide with an acute oral LD_{50} to rats > 2000 mg/kg, is being developed for use against insects that attack stored products. In preliminary studies in which water emulsions prepared from emulsifiable concentrates containing 0.5 kg AI/liter (4.17 lb/gal) (LaHue 1975) and 0.6 kg AI/liter (5.0 lb/gal) (author's unpublished data) were applied to wheat and shelled corn at rates of 5, 10, and 20 ppm, the 5 ppm dose gave satisfactory initial kills and short-term protection. This dose did not, however, give the control and protection needed for 12 mo of storage. Consequently, studies were undertaken to determine the length of protection from attack by 4 species of laboratory reared stored-grain insects provided by the application of doses ranging from 1–10 ppm. Pirimiphos-methyl EC (experimental formulation YF 6522 containing 0.84 kg AI/liter) was applied as an emulsion to 'Scout' variety hard winter wheat.

MATERIALS AND METHODS.—Cleaned 1973 crop wheat was tempered to 12.5% moisture by drying with forced air at 40.5°C after the source lots (13.8% moisture) were removed from cold storage. The wheat was allowed to equilibrate in 0.15-m^3 plastic-lined covered drums for 28 days. Then, 1000-g lots were placed in 3.8-liter large-mouth glass jars for treatment.

Emulsions prepared immediately before use by diluting EC with neutral distilled water (such that a 1-ml application dispersed the calculated dose) were kept in constant agitation at 26.7±0.6°C during the application to the wheat (temperature of 26°C). Applications were made with 1-ml volumetric pipettes to the inside wall of the 3.8-liter glass jars above the grain level while the jars were turning on a 33-rpm turntable. Immediately after application, the jars were placed on a roller for 1 min and then were rotated for 15 min on a mechanical end-over-end tumbler to thoroughly mix the insecticide with the grain. All treatments were replicated 4 times; sufficient wheat was treated to provide necessary samples for all toxicity exposures conducted during the 12-mo study and for all residue analyses. The treated 1000-g lots were combined, 2/jar, for storage at 26°±1°C and 60% RH. The jars were covered with lids during storage and were kept in total darkness ca. 75% of the storage time.

After the required aging period, 250-g samples of wheat were removed from each replication and placed in 473-ml glass mason jars for exposure to insects.

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[2] This paper reports the results of research only. Mention of a pesticide does not constitute a recommendation for use by the USDA, nor does it imply registration under FIFRA as amended, also mention of a proprietary product does not constitute an endorsement by the USDA.

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Table 1.—Average percentage mortality of rice weevils and red flour beetles exposed for 21 days to wheat treated with increasing doses of pirimiphos-methyl (formulation YF 6522).

Dose (ppm)	Posttreatment period: Months 2	3	6	9	12
	Rice weevils[a,b]				
1	89.8	91.4	97.1	71.1	75.7
2	100.0	99.3	100.0	98.9	99.5
3	100.0	100.0	100.0	100.0	100.0
Check	0.2	0	0	1.0	0
	Red flour beetles[c,d]				
1	51.6	23.3	20.2	20.1	7.6
2	78.9	82.4	78.3	51.1	13.4
3	100.0	99.5	98.6	87.4	76.5
4	100.0	100.0	100.0	99.5	100.0
5	100.0	100.0	100.0	100.0	100.0
Check	0	0	1.2	1.0	0

[a] 100% mortality was obtained for all dosages during the 1st mo of storage.
[b] 100% mortality was obtained for dosages above 3 ppm for the entire 12-mo storage period.
[c] 100% mortality was obtained with all dosages during the 1st mo of exposure except for the 1 ppm dose, which gave 97.8, 97.1, and 84.9% mortality for the 14-, and 21-day and the 1-mo exposures, respectively.
[d] 100% mortality was obtained at all dosages greater than 5 ppm for the entire 12-mo storage period.

Test jars were fitted with rings, 40-mesh screens, and filter paper lids. Ca. 100 adult insects of a species were placed in each sample. Ca. 1.0% by weight of (newly) finely ground grain from each parent sample was added back to the sample immediately before introduction of the red flour beetles, *Tribolium castaneum* (Herbst), and confused flour beetles, *T. confusum* Jacquelin duVal. Other insects used in the toxicity tests were rice weevils, *Sitophilus oryzae* (L.), and lesser grain borers, *Rhyzopertha dominica* (F.). At least 4 replicates of each treatment were exposed to each insect at each exposure for each dosage.

Insects were exposed to the treated wheat for 21 days after the treated wheat had aged 7, 14, and 21 days, and 1, 2, 3, 6, 9, and 12 mo. Mortality readings were made after 7, 14, and 21 days; however, only data for the 21-day exposure are reported. All dusts removed from the samples during the screenings made to determine mortalities were returned to the respective jars for further studies of F_1 progeny emergence and damage.

Samples for residue analyses were taken at the beginning of each exposure and were held at −20°C until analyzed.

Residue Analysis.—The primary method of the analysis for residues was adapted from Storrherr et al. (1964). Residues of pirimiphos-methyl were extracted from the wheat and were cleaned for analysis with a Tracor® MT-220 gas chromatograph as follows: 25 g of finely ground wheat were homogenized at high speed with 75 ml of acetonitrile saturated with hexane for 5 min in a Sorvall® homogenizer. The supernatant fluid was filtered through a plug of glass wool. Then 6 ml of the filtrate were cleaned by filtering through 2 g of an adsorbent mixture (5 g Norit® SC-1, 4 g MgO powder and 8 g Celite® 545) in a glass tube (10 mm IDx250 mm long) with drawn tip. Both ends of the tube had been plugged with glass wool. The residue was eluted from the column with 25 ml of 25% ethyl acetate in benzene (vol/vol) and the filtrate was collected in a round bottom, long-necked boiling flask that had a 24/40 ₮ joint. The flask was placed on a rotary evaporator, and the contents were evaporated just to dryness in a 37°C water bath. The residue was picked up in 6 ml of *n*-hexane. An aliquot of this extract was injected into the gas chromatograph.

Residues were determined by GLC at the following conditions: column—6.4 mm OD, 4 mm IDx112 cm long PYREX packed with 3% OV-1 on Chromasorb® W (100–120 mesh), AW-DMCS; column temp—190°C; injection temp—150°C; detector temp—210°C; carrier gas—60 ml N_2;min; H_2—180 ml/min; air—30 ml/min; O_2—30 ml/min; electrometer—input attenuator 10^5—output attenuator 32 (3.2×10^{-7} AFS) depending on the sensitivity desired. Retention time of pirimiphos-methyl was 85 sec. All peak areas were integrated with an Infotronics® Integrator.

RESULTS AND DISCUSSION.—LC_{50} or LD_{50} values are normally used in comparing the effectiveness of insecticides in studies of topical applications, exposure to vapors, and residual contacts with treated surface areas. However, evaluating the control of insects feeding on or infesting treated grain is quite a different matter from evaluating such kills. Therefore, we have summarized all data in tabular form.

Table 1 reports average mortalities of rice weevils and red flour beetles exposed to gradient doses of pirimiphos-methyl over a 1-yr period. All adult rice weevils were killed during the 1st mo posttreatment, and doses of 3 ppm or greater caused complete mortality for 12 mo. Adult red flour beetles were considerably more susceptible to the residues than were confused flour beetles; 4 ppm or more gave excellent kills of all adults for 12 mo. Also, mortalities resulting from 1 ppm were 97.8, 97.1, and 84.9%, respectively, for the 14-, 21-day, and 1-mo exposures.

Adult lesser grain borers were considerably more tolerant of the pirimiphos-methyl residues than were rice weevils and red flour beetles as 5 ppm were required to give complete mortality at 1 wk posttreatment; this dose was fairly effective for the 1st 6 mo (90.1% mortality) (Table 2). A dose of 6 ppm gave excellent control for 6 mo (97.0% mortality); however, 8 ppm AI or more were required to give 90% or greater control at 12 mo posttreatment. Confused flour beetle adults were also tolerant of the residues of pirimiphos-methyl (Table 2); 5 ppm AI were required to give 95.3% or greater mortalities of adults for 6 mo, and doses of 8 ppm or more were required to obtain kills above 90% at 9 and 12 mo posttreatment.

Table 3 reports residues found during the 12-mo period. Recoveries at 7 days posttreatment ranged from 73–91% and averaged 83.6%. In general, accept-

Table 2.—Average percentage mortality of lesser grain borers and confused flour beetles exposed for 21 days to wheat treated with increasing doses of pirimiphos-methyl (formulation YF 6522).[a]

Doses (ppm)	Posttreatment period								
	Days			Months					
	7	14	21	1	2	3	6	9	12
				Lesser grain borers					
1	16.0	20.0	14.5	20.7	30.8	12.4	13.6	0.2	5.9
2	38.4	33.2	21.8	37.9	38.0	24.9	22.9	13.9	15.0
3	87.1	79.0	55.4	81.4	63.6	56.2	55.7	17.0	16.5
4	97.0	90.1	90.8	90.2	92.7	89.7	84.3	45.2	42.9
5	100.0	98.8	100.0	99.8	99.3	91.2	90.1	63.4	56.5
6	100.0	100.0	100.0	100.0	100.0	96.9	97.0	72.5	70.8
7	100.0	100.0	100.0	100.0	100.0	99.5	100.0	75.0	86.3
8	100.0	100.0	100.0	100.0	100.0	99.5	100.0	93.0	95.2
9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	93.1	96.9
10	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.3	99.3
Check	0	0.4	0	1.0	1.3	0	2.2	0	2.0
				Confused flour beetles					
1	39.1	28.3	36.2	26.7	8.4	4.1	1.0	0	0
2	98.1	73.3	68.3	33.9	20.3	8.0	8.3	2.2	0
3	100.0	88.3	95.3	90.5	43.8	42.0	36.1	21.5	1.0
4	100.0	100.0	100.0	95.8	90.0	83.1	86.6	61.7	20.3
5	100.0	100.0	100.0	100.0	100.0	95.3	99.5	68.8	74.0
6	100.0	100.0	100.0	100.0	100.0	100.0	100.0	77.4	83.7
7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	85.5	84.7
8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	93.4	92.1
9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.6	97.6
10	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Check	0	0	1.2	0	0	0	0.6	0	0

[a] Avg for 16 exposures/dose/ interval.

Table 3.—Residues on composites of wheat treated with increasing doses of pirimiphos-methyl.

Dose (ppm)	Avg residues (ppm) for posttreatment period								
	Days			Months					
	7	14	21	1	2	3	6	9	12
1	0.8	0.7	0.6	0.5	0.6	0.5	0.5	0.4	0.2
2	1.6	1.3	1.0	1.1	1.2	1.2	1.0	0.8	0.6
3	2.2	2.0	1.8	1.8	1.7	1.6	1.5	1.4	1.1
4	3.1	3.0	2.8	3.6	3.6	3.6	2.6	2.6	1.5
5	4.3	4.0	3.8	3.9	3.9	4.1	3.9	3.5	3.2
6	5.4	5.2	5.2	5.2	5.1	5.0	4.9	4.8	4.0
7	6.1	6.0	6.0	6.0	6.0	5.9	5.3	5.0	4.0
8	7.1	7.0	6.7	6.7	6.7	6.5	6.1	5.8	4.8
9	8.2	7.4	7.7	7.5	7.5	6.6	5.4	5.8	6.0
10	8.9	8.9	9.0	9.0	9.0	8.1	8.2	7.9	7.2

able patterns of degradation were obtained though a few variations may be noted.

The relative effectiveness of pirimiphos-methyl to 4 species of adult stored-product insects (Tables 1–3) may be correlated with the residues found on the wheat to determine the minimum effective dosage required to kill the adults and to establish a time interval-effective dose range.

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