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Malathion on Milling Fractions of Three Varieties of Rough Rice: Duration of Protection and Residue Degradation[1,2]

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ABSTRACT

Malathion deposits of about 11, 17, and 20 ppm protected rough rice for 6 to 12 months under Gulf Coast environmental conditions. Protection lasted slightly longer in bin tests than in jar tests. Residues on rough rice greater than 8, 4, and 2 ppm were required to control confused flour beetles, *Tribolium confusum* Jacquelin duVal; lesser grain borers, *Rhyzopertha dominica* (F.); and rice weevils, *Sitophilus oryzae* (L.), respectively.

Initial deposits on rough rice were 20 ppm; deposits decreased to levels below 8 ppm within 3 months. Initial deposits on hulls were 80 ppm; deposits did not fall below 8 ppm for 7 to 11 months. Residues on bran and milled rice increased for 3 months and then declined. Residues on bran reached a maximum of 30 ppm but fell below 8 ppm in 6 to 10 months; on milled rice, maximum residue was 0.32 ppm. Varieties of bran and milled rice retained malathion in the following order: 'Belle Patna' > 'Nato' > 'Dawn.' This ranking apparently was dependent upon the relative surface area and the thickness of the covering hull on kernels of each variety.

Malathion has been extensively evaluated as a stored-grain insect protectant for corn (Womack and LaHue 1959, Floyd 1961, LaHue 1966), wheat (LaHue 1965, Gunther et al. 1958), and grain sorghum (LaHue 1967, 1969), and less extensively for a variety of other commodities since the early report by Parkin (1958) of its promise for use on food stores. The influence of formulation of malathion on its biological effectiveness on wheat has been examined (Strong et al. 1961), and critical grain moisture contents have been determined for wheat (Watters 1959, Strong and Sbur 1960, Minett et al. 1968) and for grain sorghum (King et al. 1962, Kadoum and LaHue 1969). McFarlane (1961a, b) reported on the effectiveness of malathion sprayed on sacks of rice bran.

Tilton (1961) was the first to report that malathion was effective as a protectant for stored rough rice, but he pointed out that his residue analyses and bin assay results did not correlate with bin infestation except "in a very general way." Later, Bang and Floyd (1962) evaluated malathion as a protectant for stored polished rice, and Tilton and Cogburn (1967) and Cogburn (1967) used malathion as a standard in the evaluation of other materials as protectants for rough rice. In the 2 last-mentioned reports malathion was cited as an effective long-term protectant.

Results of studies of malathion on grains other than rice, reports of stored product insects' resistance to malathion (Parkin 1965, Speirs et al. 1967), and observation by rice processors of excessive residues (>8 ppm on rice bran and hulls) have indicated a need for reevaluation of malathion for use on rice. There is a special need to examine effectiveness of malathion on rough rice under commercial storage conditions along the Gulf Coast where year-around temperatures and humidities favor insect infestation.

The original study of malathion treatments of rice by Tilton (1961) did not reveal any residues on milling fractions exceeding the 8 ppm legal tolerance where dosages of 1.0, 1.5, and 2.0 pints of 57% EC/1000 bu were used, nor did Schesser et al. (1958) find excessive residues on milling fractions of wheat at the treatment levels used. However, McFarlane (1962), after making a study of malathion sprays on bagged rice bran, questioned the standard colorimetric estimation of malathion residues (Norris et al. 1954), particularly on rice bran. Bates et al. (1962), Bates and Rowlands (1964a, b), and Rowlands and Clements (1965) found that chemical and enzymatic hydrolysis of rice bran oil to free fatty acids interfered with the colorimetric estimation of malathion even when gross amounts were applied immediately before analysis. Their reports indicated that even very brief storage of bran intended for analysis would result in interference with colorimetric estimation, and they described a method of counteracting the interfering substances. The reports cast serious doubt on the validity of Tilton's (1961) report of no excessive residues on any milling fractions of rice as the colorimetric method was used in his analyses (personal communication); the reports also tend to substantiate industry reports (personal communications) of high residues in bran as determined by gas-liquid chromatography.

The study reported here was designed to determine: (1) the effective duration of 3 dosages of malathion in preventing infestation in small bins, (2) the levels and duration of residues on rough rice, rice hulls, rice bran, and milled rice, and (3) the effect of rice variety on levels and duration of residue.

METHODS AND MATERIALS.—Three southern varieties of rice, 'Dawn,' 'Nato,' and 'Belle Patna,' were obtained from a commercial dryer after the rice had been dried to moisture contents of 13.56–13.93%. These moisture contents are typical of southern rice when it is placed in final storage, the time at which malathion application is recommended. Each variety had been graded U.S. no. 1 rice, and had received no chemical treatment to prevent or control insect infestation.

Five replications each containing a control and treatments at 3 levels of deposit were used. Three replicates, 1 of each variety, were contained in circular metal bins 57 cm diam and 61 cm high, each holding 90.7 kg of rough rice. The remaining 2 replicates were Dawn and Belle Patna varieties and were contained in cubical cardboard bins 53 cm to a side, each holding 73.5 kg of rough rice. The bins were arranged in a randomized block design. Four extra 73.5-kg cardboard bins were filled with untreated rice and placed in each corner of the warehouse to

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be used for more frequent infestation determination. The extra control bins were used to minimize disturbance of the rice in the experimental bins in the course of monitoring infestation pressure in the warehouse. Rice weevils, *Sitophilus oryzae* (L.); lesser grain borers, *Rhyzopertha dominica* (F.); and confused flour beetles, *Tribolium confusum* Jacquelin duVal, were periodically released in the warehouse to maintain very high insect infestation in these extra control bins and to infest the experimental bins as the treatments permitted.

Malathion solutions were prepared by diluting 57% EC premium grade malathion with distilled water to form concentrations that, when applied at the rate of 90 ml/90.7 kg, would produce deposits calculated to be equivalent to 14, 21, and 28 ppm (1.0, 1.5, and 2.0 pints of 57% EC/1000 bu, respectively). Actual deposits were ca. 11, 17, and 20 ppm. Rice for each metal bin was treated in 3 equal lots (while being mixed in a cement mixer) with 30 ml of the appropriate concentration of chemical applied to each. Rice for each cardboard bin was treated in 2 aliquots with 36.45 ml of the appropriate concentration of chemical applied to each. A sprayer modified from that described by Hills and Taylor (1950) to hold a larger amount of chemical and equipped with a TeeJet® TXSS1 ConeJet® tip operated with an air pressure of 30 psi was used. Each lot was mixed for 10 min and transferred to the appropriate bin.

The relative humidity in the warehouse in which the bins were held was maintained at 60% throughout the test. The temperature of the rice was 27°C at the

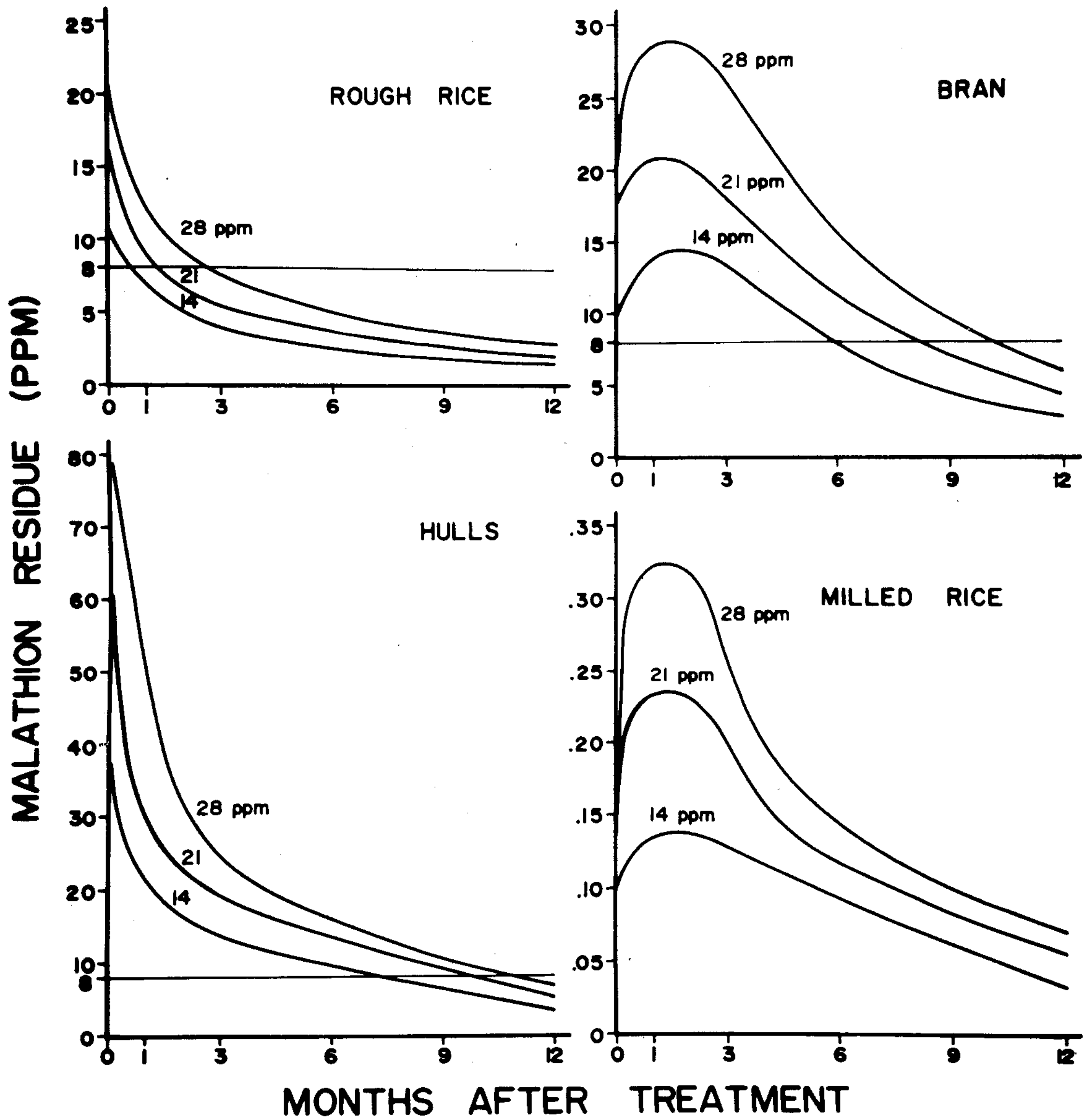

FIG. 1.—Malathion residues in milling fractions and in rough rice treated at 3 dosage levels. (Legal tolerance is 8 ppm.)

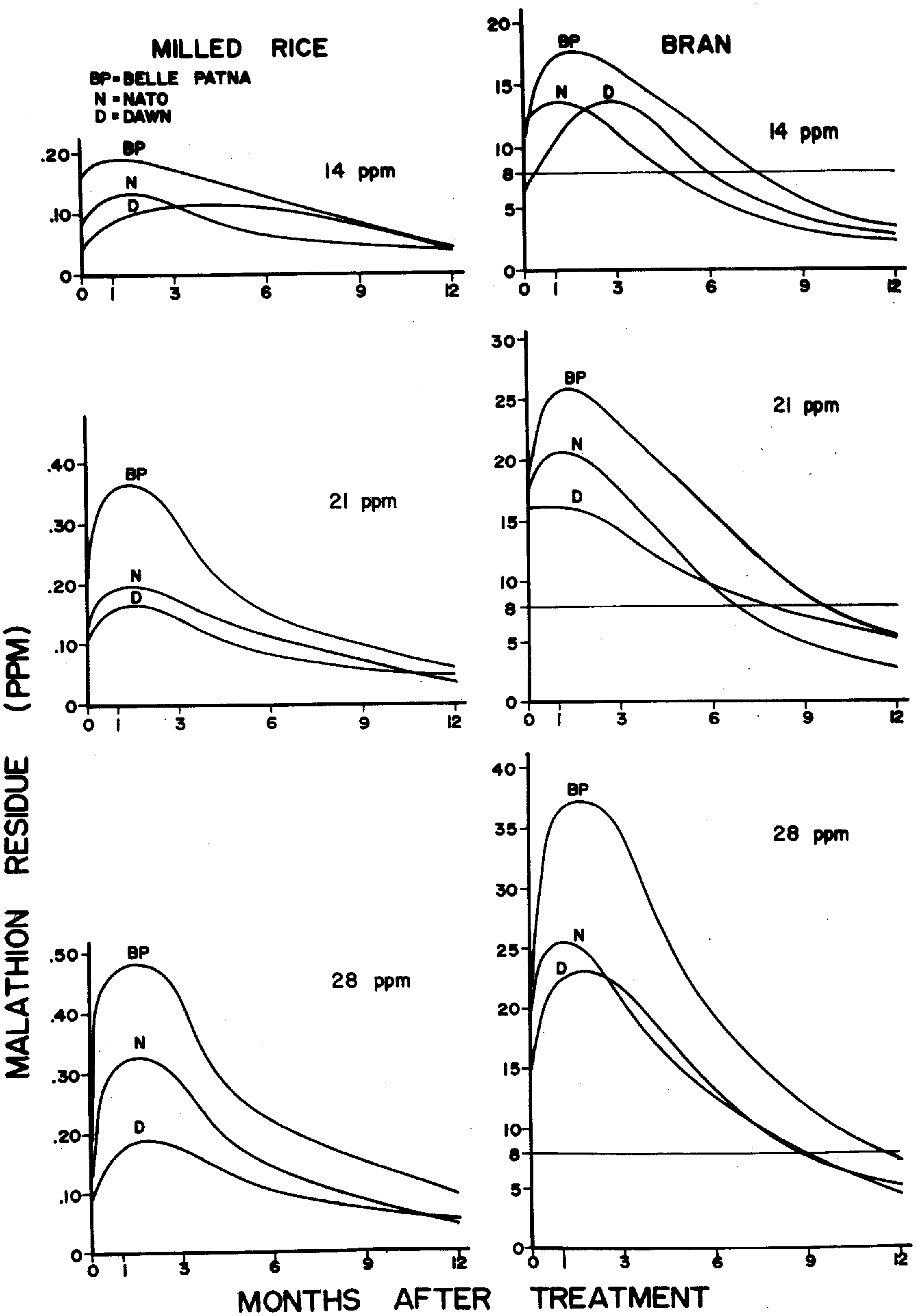

FIG. 2.—Malathion residues in bran and milled rice from 3 varieties of rough rice each treated with 3 dosages of malathion. (Legal tolerance is 8 ppm.)

Table 1.—Mortality of adults and reduction of progeny of insects introduced into 150-g subsamples of treated rice at specified intervals after treatment with malathion.[a]

Insect[b]	Mortality (%) with initial deposit of (ppm)			Progeny reduction (%) with initial deposit of (ppm)		
	11	17	20	11	17	20
			Immediately after treatment			
CFB	100	100	100	100	100	100
LGB	100	100	100	100	100	100
RW	100	100	100	100	100	100
			1 month after treatment			
CFB	84	97	98	100	100	100
LGB	100	100	100	100	100	100
RW	100	100	100	100	100	100
			3 months after treatment			
CFB	75	96	88	100	100	100
LGB	98	100	100	100	100	100
RW	100	100	100	99	100	99
			6 months after treatment			
CFB	46	46	70	100	100	100
LGB	96	100	100	77	77	98
RW	100	100	100	99	100	100
			9 months after treatment			
CFB	52	78	79	100	100	100
LGB	66	87	95	86	93	98
RW	98	100	100	84	96	99
			12 months after treatment			
CFB	30	53	87	50	100	100
LGB	0	24	49	34	68	73
RW	51	76	96	0	0	56

[a] Separate 150-g samples were infested with 50 adults (average age 2 weeks) of each insect. Mortality determinations were made after 3 weeks and progeny reduction determinations after an additional 7 weeks. Each value is the average of 3 replications. All samples were held at 27°C and 60% RH.
[b] CFB = confused flour beetle, LGB = lesser grain borer, RW = rice weevil.

time of treatment, and the warehouse temperature was programmed to change at monthly intervals to simulate average rice-bin temperatures along the Gulf Coast from September through August. The temperatures for months 1 through 14 were: 27, 24, 21, 18, 15, 18, 21, 24, 27, 30, 30, 30, 27, and 27°C. Temperatures in the small bins of rice required approximately 2 weeks to equilibrate with changes in warehouse temperature.

Samples of 2000 g were drawn from each metal bin of rice the day after treatment and after 1, 3, 6, 9, and 12 months. Half of each sample was shelled with a McGill sample rice sheller and milled with a McGill no. 3 sample rice mill. The milled rice was aspirated to remove all loose bran, and the bran was sifted through a 30-mesh sieve to remove broken rice kernels and to break up caked portions of the bran. The hulls, bran, milled rice, and 500 g of the remaining portion of the rough rice sample were submitted as coded samples for GLC residue analysis.

The remaining 500 g of each sample were sifted to determine the nature and extent of insect infestation and then divided into three 150-g subsamples. The subsamples were placed in 0.473-liter jars covered with a filter-paper cap. They were infested with 50 rice weevil adults, 50 lesser grain borer adults, and 50 confused flour beetle adults, respectively. Insects averaged 14 days old when introduced. These subsamples so infested were held for 3 weeks before mortality counts were made. After mortality counts were made each subsample was held an additional 7-week period to determine the extent of progeny development. All test insects were reared, and infested subsamples were held at 27°C and 60% RH.

The rice in the 2 replicates contained in cardboard bins was sampled at the same intervals, but only for the extent of insect infestation. Samples of 2000 g from each bin were sifted for this purpose.

Results and Discussion.—Fig. 1 presents residue data for rough rice and its milling fractions. With each treatment, residues on rough rice decreased to levels below the 8 ppm legal tolerance within 3 months after treatment. However, the residue levels on the 3 milling fractions showed marked contrast. Those on the hulls exhibited the same trend of a sharp decrease through time, but required approximately 7–11 months to drop below the 8 ppm legal tolerance. Residue levels on bran and milled rice were comparatively low immediately after treatment, but increased sharply during the initial 3 months before starting a gradual decline. Levels on bran required 6–10 months to decrease to the 8 ppm legal tolerance. Although residues on milled rice showed the same trends as did residues on bran, the actual residue levels for milled rice never approached the legal tolerance.

Fig. 2 graphically illustrates the varietal differences noted in the rate and extent of malathion penetration and persistence in the bran and milled rice. No differences were noted among the varieties on the hulls or rough rice. In each treatment level and in both bran and milled rice, the rate of penetration of the malathion and the duration of retention of residues in each fraction by rice variety was Belle Patna > Nato > Dawn. This ranking appeared to be a function of the thickness and surface area of the rice hull for each variety. Samples of 1000 g of rough rice of each variety were shelled to determine the weight of the hull fractions of each. Averages were 187.5, 191.8, and 218.4 g, for Belle Patna, Nato, and Dawn, respectively. Though only a slight difference is noted between the weights of Nato and Belle Patna hulls, when the difference in kernal shape of the two is considered (Belle Patna= long grain, Nato=medium grain), this small difference combined with the difference in surface area appears to be of great significance. Dawn is a long-grain variety exposing a relatively large surface area, but the massiveness of its hull retards malathion penetration. Very slight differences in residue levels on bran and milled rice of the different varieties occurred after 6–9 months, depending on the treatment level. The differences tended to be greater for a longer period at higher treatment levels.

The varietal effect on residue levels in bran is sufficient to cause concern over the application of malathion to varieties such as Belle Patna. At each treatment level the residue on the Belle Patna bran required approximately 2 months longer than on Dawn or Nato to decrease to the 8 ppm legal tolerance. Thus, excessive residues (>8 ppm) would persist on bran even with the 14 ppm treatment for 7 months, a period so long as to possibly render such treatments prohibitive. Although the varieties exhibit the same trends and differences in milled rice, the actual residue levels are so low that differences appear to be of little significance other than that of their correlation with levels on bran.

Table 1 presents toxicity data from jar tests of 150-g samples from small bins at intervals after treatment. After 3 months, malathion at all treatment levels ceased to be effective against adult confused flour beetles. Although progeny developed at 6 months after treatment in lesser grain borer tests, mortality of adults remained high for 9 months. Rice weevil progeny began developing at 9 months, but adult mortality continued for 12 months. Initial mortality, progeny development, and mortality of adults and progeny during the test period were about the same in the 3 varieties of rice. Residues on rough rice greater than 8 ppm appear to be required for confused flour beetle control, greater than 4 ppm for lesser grain borer control, and approximately 2 ppm for rice weevil control.

Bin infestation data suggest a longer than 12-month duration of effectiveness against each insect. Although infestation pressure was maintained in the warehouse containing the test bins, only minimal infestation could be found even in the lowest treatments at the 12-month examination. Table 2 presents infestation data at 9, 12, and 14 months. Because of the low infestation level in all treated bins at 12 months in contrast with the higher infestation level in jar toxicity tests it was suspected that some "mass effect" which could not take place in jar tests might be exerted in the larger bins of rice. Such an effect could involve repellency rather than toxicity and could involve insects' leaving the grain. Therefore, to determine the status of the treatments at 12 months, 150 rice weevils, lesser grain borers, and confused flour beetles were introduced directly onto the grain surface of each bin. This created a condition in which insect introduction was known, but in which confinement was absent, and in which the effect of the treatment on the establishment of an infestation in the bins might be determined by subsequent sampling.

All treatments became infested within 14 months (Table 2). Although all treatments were only minimally infested at 12 months, the malathion present then was not sufficient to control the insects that were introduced on the grain surface. The treatment levels in the larger grain mass may have been sufficient to repel free-moving insects for a slightly longer period.

The 11- and 17-ppm treatments became ineffective during the 9- to 12-month period. The infestation data then indicate that the treatments are slightly more effective in small bins than in jars, but that the maximum duration of effectiveness is 6–12 months, depending on the dosage used.

Table 2.—Live adult insects per 1000 g from small bins of treated rice at 3 time intervals after treatment with malathion.[a]

	Initial malathion deposit (ppm)			
Insect	0	11	17	20
	9 months after treatment			
CFB	0	0	0	0
LGB	1.1	0	0	0
RW	123.5	0.5	0.1	0.4
FGB	1.1	0	0	0
	12 months after treatment			
CFB	0.9	0	.3	0
LGB	79.6	0	0	0
RW	8.6	.1	.3	0
FGB	> 60.	.5	0	0
	14 months after treatment[b]			
CFB	4.2	1.6	1.4	1.3
LGB	357.7	2.3	2.0	.4
RW	4.2	5.9	1.8	.7
FGB	> 270.	4.6	.8	.2

[a] Lesser grain borers (LGB), confused flour beetles (CFB), and rice weevils (RW) were periodically released in the warehouse. Flat grain beetle (FGB) populations developed naturally. Each value is based on 5 replications, 3 using 500-g samples from metal bins and 2 using 2000-g samples from cardboard bins.
[b] LGB, CFB, and RW placed on grain surface of each bin at end of 12-month examination.

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