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Degradation Behavior of Malathion and Fenitrothion Residues on Wheat and Barley Under Different Storage Systems in Saudi Arabia

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Undesirable residue of pesticides used on grain may accumulate and persist during storage and processing to the time grain is ready to be consumed. The level of residues depend largely on the type and quantity of the chemical used, formulation in which it was aplied, temperature and moisture content of the grain during storage, procedure used in processing the grain during storage, and the length of time elapsing between application of pesticide and consumption of the food (Sinha and Muir, 1973; Quinlan *et al.*, 1979; Watters and Mensah, 1979; Abdel-Kader and Webster, 1980; and Dikshit, 1985).

Consequently, the objective of this study, was to obtain kinetic data on the degradation behaviour of the commonly used insecticides malathion and fenitrothion on stored grain and the influence of storage system in the degradation rate.

MATERIALS AND METHODS

Gram samples (50 kg of each) of wheat and barley, not previously contaminated with any insecticides, were treated with malathion 57% EC[S-1,2-bis(ethoxycarbonyl) ethyl 0,0-dimethyl phosphorodithioate] and / or fenitrothion 50% EC (0,0-dimethyl 0,4-nitro-m-tolyl phosphorothioate) at the rate of 8 ppm. Treated grain were stored in three replicates under different types of storage systems, i.e. non-aerated system, non-aerated with silica gel system, open storage system (Saudi system) and plastic sacks system. These systems were constructed at King Faisal University Experimental Station, Saudi Arabia.

A representative samples (one kilogram) of stored grain were taken from each treatment at different intervals after the application of insecticides (i.e. 7, 14, 30, 90 and 150 days). Samples were ground, then 3 sub-samples (100 g of each) were extracted and cleaned-up according to the method of FDA, 1979.

Determination of malathion and fenitrothion residues were carried out by Shimadzu gas chromatography (GC-16A) equipped with flame photometric detector (FID). For the quantification of the residues, a glass column 2m x 3mm i.d., packed with 1.95% OV-17+1.5% OV-210 on Gas Chrom WHP 80/100 mesh was used. Column temperature: 220°C detector temperature: 250°C injector temperature; 230°C and carrier (N) flow rate: 60 ml/min. $H_2$43 ml/min at 0.7 kg/cm^2 pressure and air 50 ml/min at 0.6 kg/cm^2 pressure. Data were confirmed on a glass column 2 m x 3 mm i.e., packed with OV-17 and QF-1 (mixed phase) 11% on 80/100 mesh Gas Chromosorb Q. Column temperature: 180°C injection/detector temperature: 250°C. The average rates of recovery at spiked samples ranging from 0.5 to 4 ppm were 92 for malathion and 90.7 for fenitrothion. The residues were corrected according to the rate of recovery. The data were subjected to statistical analysis by the method of Timme and Freshe (1980).

RESULTS AND DISCUSSION

As results in Table 1 show, the time elapsed from treatment proved influencial on the persistence pattern of used insecticides on wheat. The longer the period after treatment was the higher the degradation of insecticides. However, the pattern of degradation was varied according to the type of insecticide and storage system. The levels of insecticide residues recovered from treated wheat revealed that fenitrothion more persistant than malathion on wheat under all storage systems. In terms of figures, the dissipation rate of malathion and fenitrothion after 7 days from treatment were 23.7 & 13.7, 18.7 & 11.2, 20.0 & 13.7 and 16.2 & 12.5% at non-aerated, non-aerated + silica gel, open and plastic sacks systems, respectively. The same trend in the decline of residues of each insecticide was confirmed with all different intervals (i.e. 14, 30, 90 and 150 days) after treatment. On the other hand, all parameters in Table 2 indicated the role of chemical nature of isecticides and storage conditions on the initial deposits and the degradation of residues of the two insecticides. The intercepts of degradation lines (A) of malathion and fenitrothion (Fig. 1) leads to the conclusion that fenitrothion gave higher initial deposits than malathion. Based on the half-life periods (T/2) the degradation of the two tested insecticides on wheat under the different storage systems could be arranged descendingly as follows:

Malathion : open (47.15) - non aerated (49.75) - plastic sacks (52.68) -
non aerated + silica gel (55.02).
Fenitrothion: plastic sacks (54.33)-non aerated (60.68) - open (72.44)
- non aerated + silica gel (78.53).

Considering of the coefficient of determinations (r^2) the dependence of the logarithm of residues on time was obviously demonstrated for both insecticides at all types of storage systems. This show dependent pseudo-first order reactions for the degradation behaviour of malathion and fenitrothion on wheat. The slope of degradation lines (B) and the degradation rates (K) showed that in spite of difference of storage system the residue pattern of malathion on wheat followed that of fenitrothion. It could be predicted that the final residues of malathion or fenitrothion after 6 months from storage under all types of storage systems should be less than the maximum residue limits (MRL's).

Data concerning the residue levels and statistical quantities of the degradation of

Table 1. Residues of malathion and fenitrothion on wheat under different storage systems.

Storage systems	Days after treatment	Malathion		Fenitrothion	
		Residues (ppm)	% dissipation	Residues(ppm)	% dissipation
Non-aerated	7	6.1	23.7	6.9	13.7
	14	5.3	33.7	5.7	28.7
	30	2.2	72.5	4.2	44.5
	90	1.6	80.0	2.6	67.5
	150	0.7	91.2	1.2	85.0
Non-aerated + silica gel	7	6.5	18.7	7.1	11.2
	14	5.4	32.5	6.2	22.5
	30	3.7	53.7	5.9	26.2
	90	2.6	67.5	4.3	46.2
	150	0.9	88.7	1.8	77.5
Open (Saudi system)	7	6.4	20.0	6.9	13.7
	14	5.9	26.2	6.5	18.7
	30	4.5	43.7	4.9	38.7
	90	1.8	77.5	3.7	53.7
	150	0.8	90.0	1.6	80.0
Plastic sacks	7	6.7	16.2	7.0	12.5
	14	6.1	23.7	6.4	20.0
	30	5.0	37.5	4.8	40.0
	90	2.4	70.0	3.2	60.0
	150	1.0	87.5	1.0	87.5

Table 2. Statistical quantities and methmatical evaluation of the degradation of malthion and fenitrothion on wheat under different storage systems.

Parameter	Non-aerated		Non-aerated +silica gel		Open (Saudi system)		Plastic sacks	
	M	F	M	F	M	F	M	F
Intercept of degradation lines (A)	0.7324	0.8312	0.815	0.8838	0.8493	0.8647	0.8707	0.89
Slope of degradation line(B)	-0.006	-0.005	-0.005	-0.004	-0.006	-0.004	-0.006	-0.006
Degradation rate (K)	0.0139	0.0114	0.0126	0.0088	0.0147	0.0096	0.0132	0.0128
Coefficient of determination (r^2)	0.9017	0.9830	0.9603	0.9424	0.9989	0.9626	0.9983	0.9612
Half-life (T/2, days)	49.75	60.68	55.02	78.53	47.15	72.44	52.68	54.33

M: Malathion, F: Fenitrothion

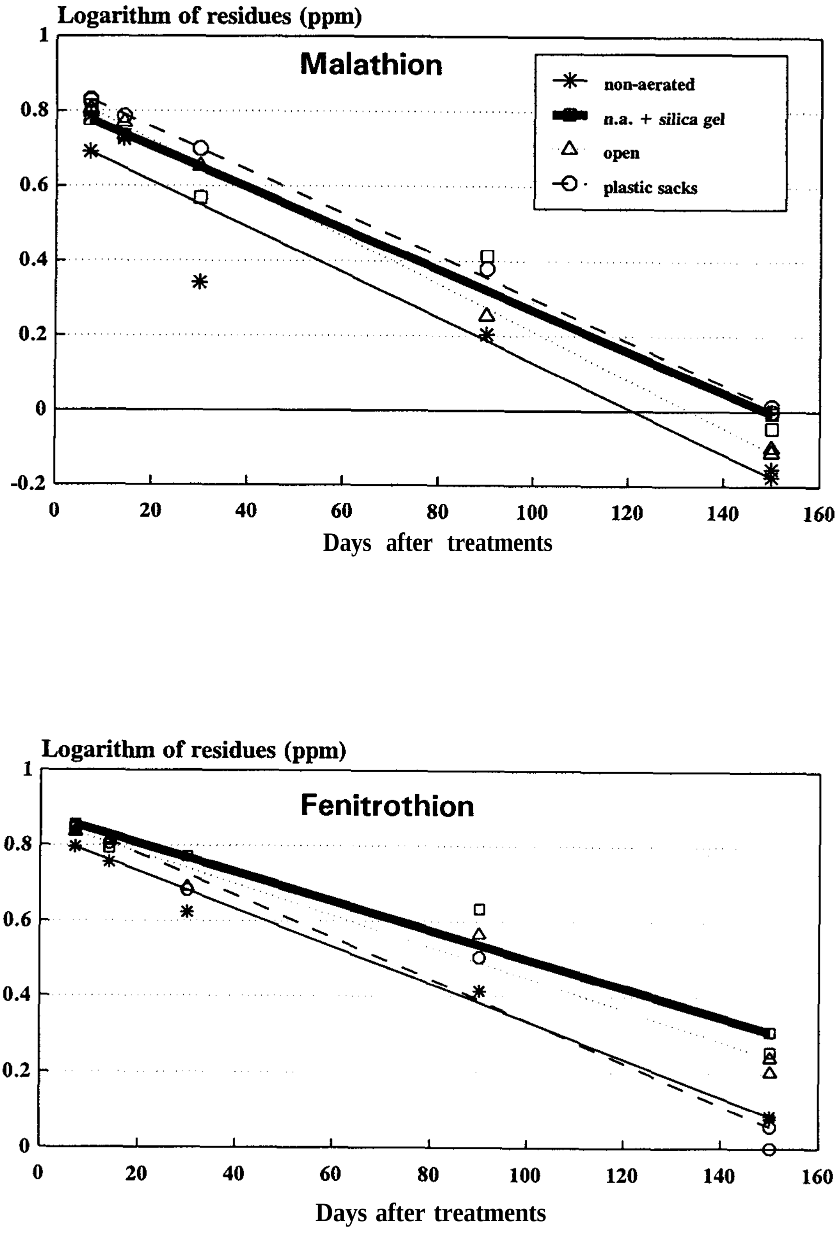

Figure 1. Degradation lines of malathion and fenitrothion on wheat under different storage systems

Table 3. Residues of malathion and fenitrothion on barley under different storage systems.

Storage systems	Days after treatment	Malathion		Fenitrothion	
		Residues (ppm)	% dissipation	Residues(ppm)	% dissipation
Non-aerated	7	6.1	23.7	6.8	15.0
	14	5.0	37.5	5.2	35.0
	30	2.1	73.7	3.7	53.7
	90	1.3	83.7	2.1	73.7
	150	0.6	92.5	0.7	91.2
Non-aerated + silica gel	7	6.5	18.7	7.1	11.2
	14	5.1	36.2	5.8	27.5
	30	4.2	57.5	5.5	35.0
	90	3.6	55.0	3.9	51.2
	150	1.1	86.2	1.4	82.5
Open (Saudi system)	7	5.9	26.2	6.7	16.2
	14	5.4	32.5	6.0	25.0
	30	4.0	50.0	4.5	43.7
	90	2.1	73.7	3.2	60.0
	150	0.9	88.7	1.1	86.2
Plastic sacks	7	6.0	25.0	6.4	20.0
	14	5.1	36.2	5.9	26.2
	30	4.0	50.0	4.3	46.2
	90	2.9	63.7	2.7	66.2
	150	0.5	93.7	0.6	92.5.

Table 4. Statistical quantities and methmatical evaluation of the degradation of malathion and fenitrothion on barley under different storage systems.

Parameter	Non-aerated		Non-aerated +silica gel		Open (Saudi system)		Plastic sacks	
	M	F	M	F	M	F	M	F
Intercept of degradation lines (A)	0.7207	0.8273	0.8194	0.8778	0.8017	0.8565	0.8469	0.8765
Slope of degradation line(B)	-0.007	-0.006	-0.005	-0.004	-0.006	-0.005	-0.007	-0.007
Degradation rate (K)	0.0151	0.0147	0.0107	0.0103	0.0129	0.0117	0.0157	0.0155
Coefficient of determination (r^2)	0.9138	0.9788	0.8974	0.9369	0.9961	0.9581	0.90521	0.9492
Half-life (T/2, days)	45.99	47.29	64.62	67.55	53.86	59.24	44.13	44.64

M : Malathion, F : Fenitrothion.

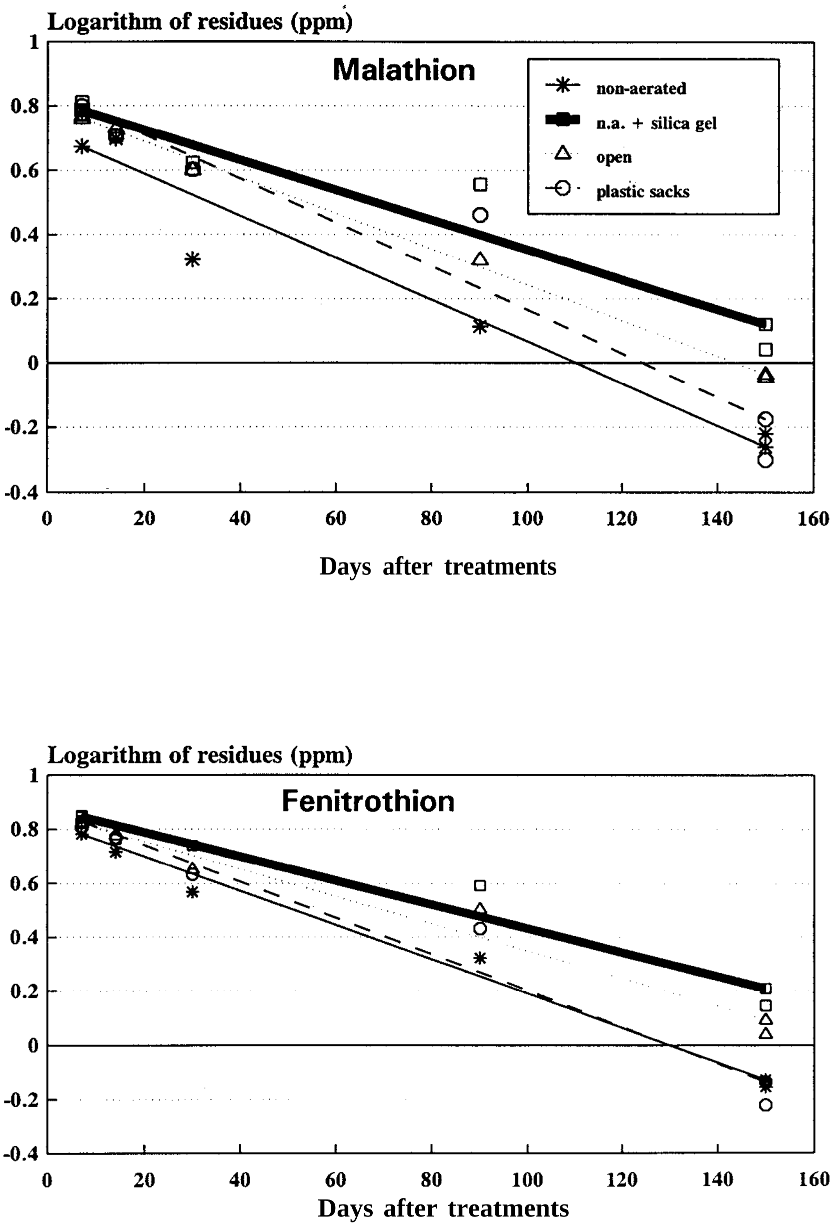

Figure 2. Degradation lines of malathion and fenitrothion on barley under different storage systems

malathion and fenitrothion on barley under different storage systems are tabulated in Tables (3-4) and graphically illustrated in Fig. 2. Residue analysis showed a gradually increasing percentage dissipation of both insecticides on barley. The dissipation of malathion was slightly higher than fenitrothion under all types of storage systems. The dissipation rate of malathion after 150 days of storage ranged from 86.2 to 93.7%, whereas, it ranged from 82.5 to 92.5% with fenitrothion. The half-life periods (T/2) were 45.99, 64.62, 53.86 and 44.13 days for residues of malathion on barley stored under non-aerated, non-aerated-tsilica gel, open and plastic sacks, respectively. The corresponding values of T/2 for fenitrothion were 47.29 67.55, 59.,24 and 44.64 days, respectively. It could be arranged the degradation of the two insecticides descendingly as follows:
Malathion: plastic sacks - non aerated - open - non aerated + silica gel.
Fenitrothion: plastic sacks-non aerated-open-non aerated+silica gel.

It is clearly interesting to notice the same pattern in the arrangement of the degradation of residues of both insecticides with the fourth storage systems. The slope of degradation lines (b) and the degradation rates (K) confirmed that the residues of malathion on barley stored under such condition followed that of fenitrothion. On the other hand, the final residues predicted after 6 months from storage should be less than the maximum residue limits (MRL’s)

Reviewing the obtained data it could be concluded that the residue pattern of malathion on wheat or barley followed that of fenitrothion under all storage conditions. These are in agreement with Abdel-Kader and Webester (1980) who reported that fenitrothion residues were slightly more stable than malathion in stored wheat under Canadian storage conditions. Also, Abdel-Kader (1982) reported again that fenitrothion being somewhat more persistant than malathion on hard red spring wheat. The degradation pattern of both insecticide residues was influenced by the type of storage systems.
In general, the degradation of the two insecticides was relatively lower at non-aerated + silica gel system than the other systems. It may be due to the increasing breakdown of the insecticides with the increasing of moisture content.

The final residues of malathion and fenitrothion on wheat or barley predicted under such storage systems after 6 months should be less than the maximum residue limits (MRL’S).These data are in agreement with Kane and Green (1968) Masud and Zaki (1976) and Hayari *et al.* (1977).

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